METALLURGIA
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METALLURGIA

Magnesium and the Future

JUST as industrial preparations for war had to be started long before large-scale fighting began, so also the industrial preparations for peace must be begun in plenty of time before the fighting ends. That many metal producers are looking ahead and endeavouring to prepare plans for post-war reconstruction is generally appreciated, and it is important that this aspect should not be overlooked with regard to magnesium and its alloys, and in this respect a recent contribution* by Mr. G. Goddard is noteworthy. Although first isolated as a metallic element early in the 19th century, magnesium was not used structurally until about 1909. Like most pure metals, magnesium is soft and has low mechanical strength, and only after continuous research with alloying elements to improve its strength characteristics was it possible to take advantage of the very low specific gravity of this metal as a structural material. Since 1909, a considerable number of magnesium alloys have been patented ; the majority, however, have proved valueless for practical purposes, about a dozen alloys now finding more general application. These latter alloys, according to Goddard,* have mainly been developed since 1920. Prior to this time magnesium was used principally for the familiar pyrotechnic purposes. The period 1920-26 was one of intensive development in which melting and working processes were developed on a commercial scale.

Initial work on the development of magnesium-base alloys was carried out in Germany, but since then considerable research and development work has proceeded in most industrialised countries, notably in the United States and Britain, and a range of these alloys has been developed which are in regular production for many applications. Since early in the war production has been limited to applications for war purposes, and production has been greatly augmented to meet pressing demands, especially for use in aircraft.

In the near future it is probable that orders will be issued lifting some of the restrictions on the use of magnesium and enable it to be used to replace other metals in short supply, to improve products, or to be applied in preparation for peace-time industrial activities. Indeed, since magnesium is now in easier supply in the United States an order has already been issued in that country removing restrictions on the use of magnesium in making products which are already allowed to be made in other metals.

It must be emphasised that nothing should be done to interfere with war production. With man-power shortage and the tendency for some essential production programme to lag,

it is obvious that there can be very little in the way of expanded civilian production in the immediate future. But in the interest of war production itself, and for the protection of the entire economy, it is essential to prepare now for the return to civilian production.

As Goddard states, the present war has brought about important changes in the production position, although in this country and in Germany there seems to have been relatively little change from the point of view of widened applications. In this country, for various reasons, there was a severe shortage of magnesium until about twelve months ago. This led to the discouragement of the applications of magnesium and the imposing of a definite ban on new applications. Much more magnesium is now becoming available in this country, and the enormous productive capacity established in America has made all the difference to the applicational picture. The maximum possible use of magnesium alloys in aircraft, to enhance their performance, is now a Government policy, and development work is proceeding rapidly. Some consideration is probably being given to post-war applications. In the United States the "Use Magnesium" campaign has been in progress longer than it has here, and this, combined with the generally more "adventurous" policy of American engineering firms, has led to magnesium applications which are not known in this country. It has been stated that this applies particularly to uses in radial engines.

For aircraft and allied industries it is obvious that there is a very great field for increased magnesium alloy applications based on the wider and more imaginative use of the existing alloys. This question is bound up with that of "technical education" of the designer and close collaboration between the specialists and the designer and user. This collaboration should take place at the earliest possible stage in the design of the new part for magnesium alloy. However, it is evident also that even greater increases in magnesium alloy applications would be possible if the following conditions were fulfilled :—

(a) If higher proof stress in the as-cast material could be realised.

(b) If the alloys had higher strengths, including fatigue strengths, at elevated temperatures.

(c) If the alloys had reduced notch sensitivity.

(d) If wrought alloys of increased workability were available.

(e) If alloys with greatly increased corrosion resistance were available.

(f) If alloys (cast or wrought form) with increased strength under compression were available.

(g) If the metal itself has good resistance to hot tearing, the alloys would possibly be superior to aluminium

from the die-casting point of view. Of these (*a*) and (*b*) are probably the most important.

Considerable work has been carried out aimed at the evolution of a casting alloy with a high-proof stress. This has involved the examination of magnesium-base alloy systems containing additions of silver, aluminium, barium, bismuth, calcium, cadmium, cerium, copper, lithium, nickel, lead, antimony, silicon, tin, thallium, tellurium and zinc, either singly or in various selected combinations. These and other combinations are still under investigation.

It must be remembered that Mr. Goddard is referring more particularly to applications for magnesium-base alloys in aircraft and allied industries, but many industrial applications, in which service conditions are not so severe, will develop, and mention is made of binoculars, book covers, scientific instruments, drills, road rammers and in reciprocating and rotating machines, such as compressors, pumps, textile and cigarette machines. As in the development in applications for aluminium-base alloys, it is important that magnesium-base alloys should only be used when they show distinctive advantage over other alloys for a particular purpose.

* " Notes on Magnesium Alloy Applications in Aircraft and Allied Industries and on Alloy Compositions." *Magnesium Review* and Abstracts, 1944, vol. iv., No. 2, pp. 35-44.

Tantalum as a Surgical Metal

THE metal tantalum possesses characteristics which make it especially valuable in the manufacture of many types of laboratory accessories. It is not tarnished in air or attacked by acids, except hydrochloric. Its tensile strength is about $2\frac{1}{2}$ times that of platinum, but it is very ductile and readily worked, and for a number of years it has been applied in the construction of certain parts of chemical equipment, for which purpose it has been rolled into very thin sheet Its melting-point is given as 3,027° C. It is a strong carbide-forming element when used in small amounts as an alloy in steels.

The recent announcement by Dr. Gustav S. Mathey, president of the Johnson and Johnson Research Foundation in New Brunswick, indicates that supplies of tantalum which have been reserved for surgical purposes can now be partially released for civilian use. This element, usually found in association with niobium, is described as a blue-grey metal about one and a half times heavier than lead ; it is capable of forming almost invisible thin wire and also sheets and plates as thin and pliable as paper. It was named after the mythological Tantalus, because it proved difficult to extract from the mineral containing it.

Initial experiments in the application of tantalum for surgical purposes were carried out at Vanderbilt University in Tennessee by Doctors J. C. Burch and J. Carney. Research is also in progress at the University of California, Montreal Neurological Institute in Canada, Northwestern University, the University of Chicago, Columbia University, the U.S. Naval Medical Institute, and by a number of individual scientists.

Results of work already carried out indicates that tantalum is especially useful to the surgeon and for some time it has been used by military surgeons to restore mangled bodies, faces and heads, which in previous wars have caused life disfigurement. The great surgical value of tantalum is its inertness ; it causes no irritation to tissue and there is no corrosion.

Tantalum wire, used as thread to sew wounds, is so thin that it leaves no scars. This wire is used to sew together the ends of severed nerves, while cuffs made of the metal protect the healing nerves. An unusual and scientifically puzzling property of tantalum is that, while ordinarily living tissues try to keep away from foreign substances, the tissues, including bones, cling so closely to tantalum that there is a difference of opinion as to whether or not they may actually be attaching themselves to the metal.

In the form of plates, tantalum is being used to restore normal shapes to skulls, where the bone has been partly shot away. The metal is so malleable that the plate can be given its final shape beside the operating table ; this is especially important when it is to replace bone in the skull.

Quality Control Saves Labour and Materials

QUALITY control of manufactured products by use of statistical methods, developed from experience in a large number of industries, has resulted in substantial saving of labour and materials in many war plants. Use of a control chart determines the degree of inspection that should be applied to the product being manufactured, provides a basis for improvement in production and assembly methods and gives better quality assurance than can be obtained by the usual inspection methods.

The scientific approach to product quality is not merely a temporary war emergency development, but will find many important applications to post-war problems of competition for better quality and lower costs. Both large and small concerns using quality control by statistical methods have achieved remarkable results in : (1) Improving the quality of purchased materials and of plant products ; (2) reducing the wastage of labour and materials from spoilage of product, increasing rejections ; (3) decreasing inspection costs ; (4) improving labour efficiency and facilitating the use of inexperienced labour ; (5) improving producer-consumer relation.

It is noteworthy that tuition-free intensive courses in quality control are being given at various American universities, which are being attended by engineers, production executives, chiefs of inspection and other personnel of war industries and branches of the armed services, and it would seem profitable to institute such courses of study in this country.

THE July issue of the *Nickel Bulletin* contains abstracts dealing with powder metallurgy, bonding in electroplated metals, sand casting of non-ferrous alloys, testing of brake magnets, centrifugal casting methods, and creep strength of nickel-containing alloys.

Copies of the *Nickel Bulletin* may be obtained, free of charge, from the Mond Nickel Co., Ltd., Grosvenor House, Park Lane, London, W. 1.

British Electrolytic Copper Powder

By H. W. Greenwood

(*Powder Metallurgy, Ltd.*)

The economic production of electrolytic copper powder in this country has presented many difficulties and until recently the amount consumed in Britain was imported. As a result of research and development, during the last few years a satisfactory solution to the problem has emerged and electrolytic copper powder production in this country is now stabilised. The subject is informatively discussed and attention is directed to the grades available.

FOR some years before this war between 500 and 1,000 tons of copper powder were consumed annually in this country in the manufacture of porous bronze bearings and motor and dynamo brushes. All of this powder was imported from both America and Germany and no British manufacturer existed. This situation in 1937 to 1939 caused considerable concern among the consumers and several attempts were made by them to persuade various powder manufacturers in this country to erect electrolytic copper powder plants in order to replace German supplies and to take care of Atlantic shipping losses. Fortunately—very fortunately for the consumers—these losses were not so serious as had been anticipated, because it is only within the last twelve months that there has been any considerable British production. There are now at least two producers of electrolytic copper powder in this country, and at least one factory situated in the South of England is producing an annual tonnage of powder having a quality equal if not better than the American material.

Whilst it gives cause for satisfaction to hear that British manufacturers have at last entered this field, it may well be that the reader wants to know why the consumer has had to wait until war is nearly over for British supplies. Probably a certain amount can be credited to typical British inertia, but a complete explanation indicates that the metal powder manufacturers' angle was by no means a simple proposition, as the following paragraphs are intended to show.

There are few secrets in the manufacture of electrolytic copper powder and it is usually deposited in cells under conditions very similar to those employed in electrolytic copper refineries with small modifications to electrolyte composition and current densities although with considerable changes in cathode construction. As a consequence, it is a simple matter for an electrolytic copper refinery to incorporate some powder producing cells in among the large number of refined copper cathode cells. Powder has, therefore, naturally been produced in the past by the larger copper refineries in Germany and America, and taking advantage of the low cost of electricity in these plants, low overheads, and, what is most important, ability to consume anode scrap internally, waste electrolyte and oversize and undersized powder, it has been possible for such large copper refineries to manufacture copper powder at a cost but very slightly higher than that of cathode copper.

Now there are no large electrolytic copper refineries in Britain and electricity is expensive, particularly in industrial areas, such as London, Manchester and Birmingham. A British manufacturer of powder has therefore to face the problem of attempting to compete with the American market under the handicap of using a plant which is necessarily small (since the demand for copper powder in this country is small compared with American figures), which must be self-sufficient from the internal scrap utilisation point of view and which must make use of refined copper (at refined copper prices) as a raw material. These and various other commercial and technical problems are sufficient to discourage most firms from entering this field. To avoid the difficulties of this problem some attempt was made over the first two years of war to persuade the copper powder consumers to use powder made by cheaper processes, such as, for example, atomisation, but without success, because the users of copper powder have built their technique up on electrolytic powder, and it is very difficult for them, if not impossible, to change over to a powder having entirely different pressing and sintering characteristics.

From continued research and development during the last four years there has now emerged a satisfactory solution to the problem, and profitable manufacture of electrolytic copper powder in this country on a considerable scale is now stabilised, although it must be said that the success of it as an enterprise is entirely dependent upon the co-operation of consumers and the maintenance of the pre-war import tariffs on this material. One satisfactory aspect of the matter is that the solution of the problem of competing successfully with American production has necessitated such close technical study that as a result the technical control and design of the British plant and quality of the product is now probably higher than that current in America or Germany.

Whilst it is possible to produce electrolytic copper powder having a range of loading weights (apparent densities) from about $1 \cdot 8$ to $4 \cdot 0$ grammes per c.c., there is not at the moment in this country a demand for so wide a range and for most purposes loading weights from $2 \cdot 5$ to $3 \cdot 3$ are mainly required. The powder marketed by the leading British manufacturer is supplied in three main grades : (*a*) Coarse, comprising material between 40 and 100 mesh. This material has a flow factor of 100 grammes in 18 secs. through an orifice $0 \cdot 177$ in. diameter and a loading weight of $2 \cdot 2$ to $2 \cdot 6$ grammes per c.c. (*b*) Grade " M." This is the main bulk of the production manufactured to specifications of the producers of porous bronze bearings, in which 100–200 mesh averages 25–35%, $- 200 + 300$ mesh, 20–30%, and $- 300$ mesh, 40–50%. This material has a loading weight of $2 \cdot 7$ to $2 \cdot 9$ and a flow factor
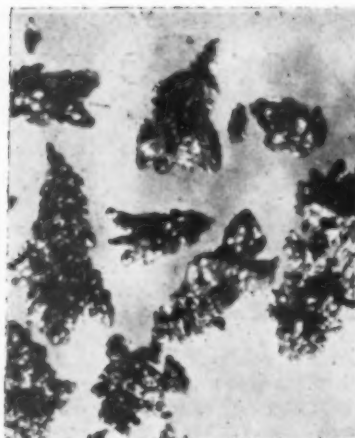
Fig. 1.—Electrolytic copper powder—40 + 100 mesh. ×66.
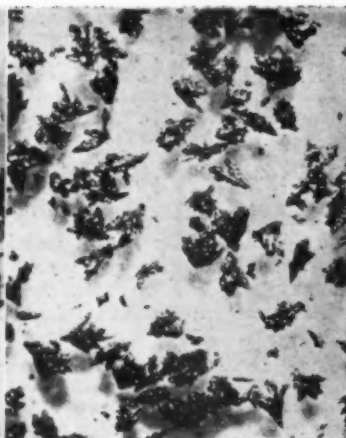
Fig. 2.—Electrolytic copper powder, Grade M. × 66.
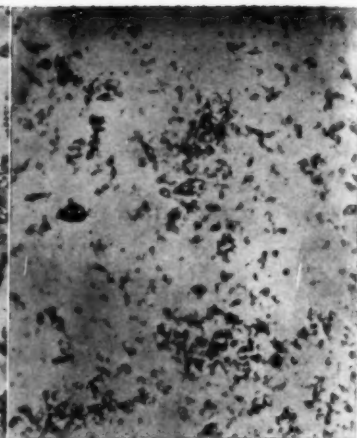
Fig. 3.—Electrolytic copper powder—300 mesh. × 66.

ranging round 100 grammes in 13 to 15 secs. This grade corresponds fairly closely to the American " B " heavy quality. This grade of electrolytic copper powder is the most generally useful material made in this country and is ideally suited for most powder metallurgy operations where a free-flowing powder is demanded. (c) Extra fine grade, approximately 100% through 300 mesh having a loading weight of 2·0 to 2·5 grammes per c.c., but no flow factor. For many powder metallurgy operations such as manufacture of diamond tools, it is desirable to use a substantially finer grade of powder than the standard " M " grade, and where absence of flow factor is of no importance this extra fine quality is the most desirable type. This quality corresponds approximately with the American " C " special grades used mainly in America for the manufacture of dynamo and motor brushes, although the British powder has a somewhat higher loading weight.

All these powders are manufactured to rigid chemical and colour specifications—for example, the loss in weight in hydrogen of the standard " M " grade being less than 0·25% with a copper content of 99·5% minimum and having a fresh salmon pink colour, not deteriorating substantially when stored for six months in a clean warm atmosphere.

In order that the reader may obtain a visual idea of these three grades of powder, Figs. 1, 2 and 3 show photomicrographs of each grade under the common magnification of 66 diameters. These photographs give a good idea of the relative particle size distributions of the three grades and also show well the feathery dendritic shape of the particles. Fig. 4 under a magnification of 600 diameters is a section of the " M " grade powder mounted in a plastic. This photograph also gives a good indication of the dendritic shape and indicates partial recrystallisation of the copper with some twinning. The central spine frequently seen down the centre of each dendrite is also well shown.

The manufacture of porous bronze bearings, motor brushes and impregnated diamond tools using copper powder has been conducted in this country for some years now. In America a considerably wider range of articles are manufactured by powder metallurgy, and these include steel-backed bearings of various types, porous metal filters, friction plates and blocks, and a wide variety of non-porous articles of all shapes and sizes in bronze and brass alloys. A considerable number of firms in this country are now experimenting with powder metallurgy with a view of initiating similar practice and further developing the art of powder metallurgy. It may, therefore, be of some use to potential manufacturers of this type if something is said about the selection and testing of various powders.

Success or failure in the operations of powder metallurgy is largely dependent upon the use of the right type of powder for the specific purpose one has in view, for upon this will depend almost entirely the physical properties of the final product and in no small degree the type of plant to be used, the conditions under which that plant will operate and whether it will operate economically or not. A number of various methods have been used in the past for the manufacture of copper powder, but, broadly speaking, only the three processes of electrolytic deposition, gaseous reduction of copper oxide and various types of atomisation of the molten metal are used commercially. Each type of powder has its natural field of application. From the point of view of powder metallurgy, however, atomised powder is of only limited use, such as in cases where no outstanding physical properties are required in the pressed or sintered compact as sometimes happens, for the manufacture of porous filter materials, and as a minor alloying addition to compacts having a basis of another metal. Atomised copper powder has, however, extensive application in other directions, such as in the chemical industry and in the manufacture of welding rods. Atomised copper consists of spheres or near spheres, and the solidity and smoothness of the particles renders the powder unnecessarily difficult to compress, so that compacts of reasonable mechanical properties are produced only in company with high die pressures and die wear.

Both electrolytic and gaseous reduced copper powders are generally used for powder metallurgy, but in this country there is a preference towards the electrolytic type, and no commercial manufacture of reduced powder is undertaken here. These powders have decidedly soft pressing properties, due partly to the

spongy and porous nature of each particle and partly to the irregular shape which leads to low loading weights. The preference for electrolytic powder instead of gaseous reduced is not entirely clear, but it is generally believed in this country that reduced powders involve slightly higher die wear and are not so stable to atmospheric oxidation.

It is useful therefore to be able to recognise each type of powder and this is best effected under the microscope. There is normally never any doubt concerning the atomised spherical or granulated type of particle, but in some cases a little confusion may arise between gaseous reduced and electrolytic types. When of ideal characteristic appearance, the reduced particles can best be described as coke-like, whilst the electrolytic particles are feathery or snow-flake dendrites as shown in the photographs. On some occasions, however, electrolytic particles may appear decidedly knobbly, and could easily be mistaken for reduced copper, whilst other samples consist almost entirely of needles. Atomised copper generally has a high loading weight between 3·5 and 4·5, but reduced and electrolytic powders normally vary between 2 and 3 gms. per c.c., the more feathery the particles the lower the loading weight. Some experience is necessary before one can be absolutely certain of the method of manufacture, and occasionally even the expert is misled. It is, for example, quite possible to produce electrolytic copper powder having a loading weight of 4·0 gms. per c.c., and atomised powder appearing under the microscope similar to reduced powder and having a loading weight of only 1·5 gms. per c.c.

Fig. 5.—Flow factor meter (Powder Metallurgy Ltd.)

Fig. 4.—Electrolytic copper powder, Grade M. × 600.

For general purposes the particle size of powders used in powder metallurgy is of two types, either all through 180 mesh or all through 300 mesh. The latter is more suited to the manufacture of non-porous compacts. For porous materials there is a tendency towards employing coarser powders, such as 120 mesh and sizes as coarse as 40 mesh have a field of application. Hot pressing work generally requires a coarse powder having only a small percentage of fines. The particle size distribution curve in the plus 300 range is best and easily determined by sieving for a constant time through a nest of sieves on a standard sieve shaking machine. Care should be taken in examining sieve specifications to note whether U.S.A., I.M.M., or B.S.S. figures are quoted, since the differences are appreciable. The finer sizes from 300 mesh to 1 micron require more complex elutriation methods of which there are many. Useful assistance in this direction can be obtained from various textbooks, such as " Micromeritics," by J. M. Dallavalle, and the books by Baeza and John Wulff. In some cases the proportion of fine powder in the region of 1 to 10 microns has a critical influence on the behaviour of the pressed compact during sintering, particularly if a liquid phase is present during the operation.

For mass production of articles by powder metallurgy on mechanical presses where the amount of powder taken per cycle is measured by volume and not by weight, it is important that the apparent density of the powder or loading weight is predetermined and maintained constant. For the manufacture of small articles on mechanical presses of British or American manufacture it is also generally necessary that the powder should have free-flowing characteristics, but it is important to recognise that such a quality can only be given to a powder at a sacrifice in some other direction, such as, for instance, in particle size distribution. To call for a free-flowing powder necessitates a comparatively coarse powder, there generally being little or no flow

in powders, of which more than 60% passes 300 mesh. When mechanical high-speed presses are not being used, free-flowing powders are quite unnecessary, and generally better results can be obtained by using finer grades of the 300-mesh type. The flow factor is an arbitrary figure obtained by taking the time required for 100 grms. to flow through a standard flow meter. This instrument is shown in Fig. 5. It consists of a cup turned from bronze and having an internal cone-shaped section, the bottom and narrowest part of which is a circular orifice of stated diameter—namely, 0·177 in. This cup is supported by a standard, and the whole is reasonably rigid, so that vibration cannot easily take place. When determining the flow factor the orifice is stopped by a finger and the powder poured into the cone, using a specific weight—for example, 50 or 100 grammes—then the time is taken with a stop-watch for the powder to flow through the orifice, and is expressed as 'the time required for the flow of 100 grammes. That is the flow factor. The flow meter is supplied with a metal cup having a capacity of exactly 25 c.c. The powder is allowed to flow into the cup until it is filled to overflowing. The metal spatula or blade supplied with the flow meter is then used to smooth over the top level with the broad brim of the cup, and the contents are then weighed. One then has the weight of 25 c.c. of powder which multiplied by 4 and divided by 100 gives the gramme/c.cm. weight, or as it is more frequently called,

the loading weight. Sometimes the loading weight is expressed as grammes per cub. in., but this seems to be a needless mixing of two systems of weights and measures, and inasmuch as practically the whole of the rest of the world uses the metric system of weights, it is preferable to express it as grammes per cubic centimetre. The three physical properties just discussed—namely, particle size, flow factor and loading weight, must always be considered together. In some respects it would be reasonable to say that they comprise the three points or factors upon which a specification for copper powder rests, and that would equally be true for many other metal powders.

The exact suitability of any type of powder to its proposed use can of course only be determined by complete laboratory tests and in the final analysis by trial runs in the works. Of tests of this type from a powder metallurgy point of view a measurement of the cold-pressing characteristics is most useful in indicating the order of pressure that will be required in use and whether high die wear is likely to be experienced or not. For this purpose small pellets should be pressed in the shape of cylinders some $\frac{1}{4}$ in. diameter and $\frac{3}{8}$ in. long and a curve plotted between density and pressure both before and after sintering. For testing procedure along these lines Baeza's book will be found most helpful.

Acknowledgment is due to Mr. M. H. Wilkes for excellent work in the preparation of the photomicrographs.

Specifications for Lead, Tin and Zinc Alloys

With the object of rationalising the whole field of non-ferrous metals and alloys, Services Schedule B.S./S.T.A. 7 was prepared. In view of its magnitude, copper and its alloys were dealt with in 1942, an additional section covering nickel and its alloys in 1943, while the present review concerns three further sections which have been added covering specifications for lead and its alloys, tin and its alloys, and zinc and its alloys, respectively.

SERVICES Schedule B.S./S.T.A. 7 of non-ferrous metals and alloys was prepared from a statement of the joint requirements of the Services for non-ferrous metals and alloys for armaments and general engineering purposes. It was drawn up by a conference of the technical representatives of the various Government Departments, together with those of several manufacturing firms convened by the Superintendent, Technical Applications of Metals, Ministry of Supply. Assistance in preparing the Schedule was also given by the British Standards Institution, the British Non-Ferrous Metals Research Association, and the Copper Development Association.

As the rationalisation of the whole field of non-ferrous metals and alloys required a survey of considerable

magnitude, and in view of the time likely to be involved, only copper and its alloys, Group 1, were dealt with in the Schedule issued in 1942. This group covers composition and properties of copper, C series ; aluminium bronzes, CA series ; gunmetal, CG series ; alloy high-tensile brass, CM series ; phosphor bronzes, CP series ;

TABLE I.—MISCELLANEOUS LEAD ALLOYS—LX SERIES.

No.	Description.	Chemical Composition.						Notes.
		Pb.	Sn.	Sb.	Cd.	Bi.	Other Elements.	
LX 1	Decoppering foil, collapsible tubes, etc.	Rem.	—	—	—	—	4·0	—
LX 2	Electro backing metal....	92–97·5	0·5–4·0	2–5	—	—	0·25°	—
LX 3	Linotype metal	82–88	2–5	10–13·5	—	—	0·25°	Freezing range for 86/3/11 alloy : 239°–246° C.
LX 4	Monotype metal	73–79	6–10	15–20	—	—	0·25°	Freezing range for 77/8/15 alloy : 240°–263° C.
LX 5	Stereo metal	70–83	5–10	14–18	—	—	0·25°	—
LX 6	Matrix alloy	28·5	14·5	9·0	—	48	—	Melting range : 120°–155° C. approx.
LX 7	Tube-bending alloy	26·7	13·3	—	10	50	—	Melting point : 70° C. approx.
LX 8	Admiralty jointing alloy..	Rem.	10–10·5	10–10·5	—	—	—	—

* Cu, Fe and As not to exceed 0·05% each.

silicon brasses and bronzes, CS series ; brasses, CZ series, and special purpose and miscellaneous copper alloys, CX series.[1] During 1943 an additional section was added to the schedule dealing with nickel and its alloys, Group 2.[2] This group covers composition and properties of nickel, N Series and nickel-base alloys, NS and NC series approved for service use. This year three further additions have been made to the schedule, and these deal with lead and its alloys, Group 3, tin and its alloys, Group 4, and zinc and its alloys, Group 5.

Lead and its Alloys

Group 3 covers the composition and properties of lead, L series ; the economy soft solders, LS series ; lead-base bearing metals, LB series ; lead antimony alloy, LA series ; and miscellaneous, LX series. The economy soft solders were issued as an appendix A to the schedule and have already been reviewed.[2] Corresponding relevant British and American specifications are also given, together with a general note on the various alloys and their uses.

Fourteen types of lead are included in the L series, and are numbered L1 to L13B. These include chemical lead ; fine-grain chemical lead ; fine-grain copper chemical lead, 0·06 to 0·07% copper ; fine-grain copper-tellurium chemical lead ; lead cable sheathing and sleeves ; lead alloy cable sheathing, 0·8 to 0·9% antimony ; lead alloy (" Admiralty ") cable sheathing, 0·35 to 0·45% tin, 0·12 to 0·18% cadmium ; lead alloy cable sheathing, 0·35 to 0·45% tin, 0·15 to 0·25% antimony ; lead pipes ; silver-copper-lead pipes ; lead alloy pipes ; and ingot lead (L13A and L13B) used for caulking and balance weights respectively. All these various types of lead are covered by British Standard Specifications, except the fine-grain chemical lead, sheet lead and ingot lead.

In the LB series two lead-base bearing metals are included, containing 7 to 12% tin, 10 to 18% antimony, 1·5% copper, and 5% tin, 10 to 18% antimony, 1·0% copper respectively, with the remainder lead. These alloys are specified in the " Economy of Tin in Plain Bearing and Bearing Metals," issued by Non-ferrous Metal Control. LB 1 is suitable for bearing surfaces working at moderate speeds and loads, and LB 2 for bearing surfaces working at moderate speeds under lighter loads and less arduous conditions than LB 1.

The lead-antimony series include ten alloys, only one—cast regulus metal LA 7, containing 8 to 10% antimony, 0·15% other elements, and having an ultimate tensile strength not less than 7,000 lb. per sq. in. and a Brinell hardness not less than 16—being covered by a British Standard Specification. The first five alloys are bullet-core material and cover the specialised requirements of the various types of bullet cores used for small arm ammunition, LA 2, which contains 0·4 to 0·7% tin, 1·4 to 1·6% antimony, and 0·15% other elements being intended to cover the use of tin-bearing scrap. Pipe and sheet material LA 6 is specified for special purposes use in chemical and electroplating plant, and cast regulus metal LA 7,

which combines good corrosion resistance with machinability, is suitable for valves, ejectors, acid pumps, plugs, pans and working parts to withstand mechanical action, chiefly abrasion. The other three alloys of this series, LA 8, LA 9 and LA 10, are for cast battery plate grids, shrapnel bullets and balloon wedges respectively, the last alloy having a high antimony content, 10 to 10·5%, in order to give required resistance to wear and abrasion in addition to strength.

The miscellaneous lead alloys included in the group are given in Table I. Decoppering foil replaces 60–40 tin-lead alloy, formerly specified for decoppering guns, and is also suitable for collapsible tubes for certain purposes. The high lead content of the electro backing metal gives a long freezing range and has the highest melting temperature of all common type metals. It is less wear-resisting, but also less brittle than LX 3, LX 4 and LX 5. The matrix alloy expands slightly on solidification, and is used as a matrix for locating punch and die parts and other purposes. Tube-bending metal is similar to Wood's metal, and is used for loading tubes for bending, being removable by immersion in water at 100° C. ; while the Admiralty jointing alloy is used for high pressure, hydraulic joint rings.

Tin and its Alloys

Three varieties of tin are specified in the T series of Group 4. These include high-purity tin, 99·9%, whose use is restricted to special applications where high-purity of metal is essential, and refined tin containing a minimum of 99·75% tin used for tinning of tinplate by hot-dipping ; anodes for electro-tinning ; tinning of bearing shells ; high-grade bronzes ; and for pure tin tubing, wire and powder. Refined tin is also suitable for collapsible tubes for certain pharmaceutical products and foods, where freedom from chemical contamination is essential. Very small amounts of hardening additions such as antimony and copper, are sometimes made to this alloy when these are not chemically deleterious to the contents of the tubes. The third variety, common tin containing a minimum of 99·0% of tin is for use for foundry work and for tinning and general purposes wherever possible.

The tin-base bearing metals—TB series—are given in Table II. The first alloy, TB 1, comes under Group 1, PB 1, and the second alloy, TB 2, under Group 2, PB 1, of the " Economy in Tin in Plain Bearings and Bearing Metals," issued by Non-Ferrous Metals Control. TB 1 is suitable for bearing surfaces working at high speeds and under heavy and especially fluctuating loads, as in the case of crankshafts and big-end bearings, etc. For bearing surfaces working at high speeds and under medium, steady or lighter, fluctuating loads, or at moderate speeds with heavy, fluctuating or steady

1 METALLURGIA, 1943, vol. 28, pp. 207–210
2 METALLURGIA, 1944, vol. 29, pp. 326–328

TABLE II.—TIN BASE BEARING METALS—TB SERIES.

No.	Description.	Chemical Composition.						Notes.
		Sn.	Pb.	Sb.	Cu.	Zn	Other Elements.	
TB 1	(A) Tin-base bearing metal, lead free. (P.B. 1, Group 1.)	80–92	0·5	7·5	4·5	—	—	Soft Grade
	(B)　　　Ditto	80–88	0·5	Sb & Cu	12 min.	—	—	Hard Grade
TB 2	(A) Tin-base bearing metal. (PB 1, Group 2.)	68–75	Rem.	6·0	5·0	—	—	Soft Grade
	(B)　　　Ditto	68–75	Rem.	10·0 min.	8·0	—	—	Hard Grade
TB 3	Admiralty under-water bearing metal	Rem.	0·5	1·0	1·0–2·0	28·5–30·5	As 0·10 Fe 0·10	—

TABLE III.—ZINC ALLOYS—ZA SERIES.

No.	Description.	Chemical Composition.												Related Specification.
		Zn.	Al.	Cu.	Mg.	Fe.	Pb.	Cd.	Sn.	Sb.	Ni.	Mn.	Si.	
ZA 1	High-purity (Copper-free) Alloy　Ingot Metal for Die-casting (Die-castings)	Rem. Rem.	3·9 4·3 (3·9 4·3)	0·03 (0·01)	0·03 0·06 (0·03 0·06)	0·075 (0·1)	0·003 (0·005)	0·003 (0·005)	0·001 (0·002)	—	—	—	—	B.S. 1004 Alloy A
ZA 2	Secondary alloy for die-casting.....	Rem.	3·9 4·3	1·0	0·03 0·06	0·1	0·007	0·005	0·003	—	—	—	—	B.S. 1141
ZA 3	Aluminium-zinc alloy	Rem.	34 40	—	0·1	0·3	Pb +	Cd +	Sn 0·03	—	0·3	0·5	0·5	D.T.D. 598
A Z5	Under-water bearing metal	56–58	—	—	—	—	—	—	28–29	14–15	—	—	—	—

loads, alloy TB 2 is suitable. While tin supplies are restricted, lead-base alloys LB 1 and LB 2 should be used, instead of these alloys where possible. Alloy TB 2 is specified for stern-tube bearings, etc.

The miscellaneous tin alloys include an alloy for cartridge lids for powder ramming, now obsolescent; tinfoil with a very restricted use for decoppering foil and for which lead foil LX 1 should normally be used, and two solders. TX 3 is a 65–35 tin-lead, low melting point (eutectic) solder for instrument work, capping shot, etc., and TX 4 a low melting point antimonial solder suitable for emergency repair work in the field. The use of both solders, which are covered by British Standard Specifications, should be severely restricted on account of their high tin content, and economy solders, LS series, should be used instead.

Zinc and its Alloys

Five grades of zinc are specified in the Z series, and four zinc alloys in the ZA series. High-purity zinc, Z 1, containing 99·99% zinc, is to British Standard Specification and is suitable for die-casting alloys, wire, foil and anodes. For high-grade brasses and other alloys, wire, zinc spraying, anodes and zinc oxide, high-grade zinc, Z 2, containing a minimum of 99·95% zinc is suggested. Z 3 zinc for rolling, foundry work, etc., contains a minimum of 98·5% zinc and 1·25% lead, and suitable uses for this metal are for sheet and strip, anodes, brass and other alloys, and zinc oxide. For some of these applications an iron content below the maximum of 0·05% is required, and contents of cadmium and other constituents may be restricted. Zinc for hot-dip galvanizing, Z 4, containing a minimum of 98% zinc, may also be used for brass manufacture, zinc dust and zinc oxide.

The four zinc alloys, the first two of which are to British Standard Specification and the third to a D.T.D. Specification, are given in Table III. The high-purity (copper-free) alloy is a high-grade die-casting alloy, not susceptible to intercrystalline corrosion or dimensional instability. ZA 2 is an economy alloy for die-castings produced from remelted castings of the high-purity alloy. On account of the increase of the permissible copper content this alloy has not the same dimensional stability nor does it retain strength at raised atmospheric temperatures to the same degree as ZA 1. This alloy must be restricted to those applications where the · maintenance of dimensional stability throughout the service life of a casting is not of primary importance. The relatively high limits for lead and tin necessitate also great care to prevent pick-up of impurities during die-casting which would take the impurity limits beyond the safe margin.

High-grade zinc, Z 2, and Duralumin scrap are used for the manufacture of the aluminium-zinc casting alloy, which is suitable only for limited applications, in which comparatively low ductility and resistance to impact can be tolerated. Its specific gravity is intermediate between that of zinc and aluminium alloys. ZA 4 is an alloy suitable for certain bearings to be used in sea-water or fresh water (stern-tube bearings, etc.). It is readily oxidised on melting, and special precautions in casting, including bottom pouring and internal water-cooling for liners over 12 in. long, are necessary to ensure soundness.

Bauxite in Jamaica

ALUMINIUM, LTD., has acquired bauxite properties in Jamaica, which give promise of being one of the important world sources of this ore of aluminium. Work carried on by this company since 1942 will lead to the opening of a mining industry and should ultimately result in the erection of a plant for the treatment of ore on the island. The company, in collaboration with the Colonial Government, is embarking on a parallel programme of agricultural development of its newly acquired lands along scientific lines with a view to increasing the self-sufficiency of the community. These new Jamaican bauxite resources will supplement the British Guiana ores on which the Canadian aluminium industry has largely depended heretofore and will provide a broader base for the expanded aluminium-producing facilities in Canada to which England, Australia and other countries have come to look as a major source of supply.

The British Fluorspar Producers

Following several delegate conferences with the Fluorspar Control of the Ministry of Supply, the Derbyshire Fluorspar Producers' Association has now enlarged its scope and become the national representative body of the fluorspar industry. The name has been changed to that of " The British Fluorspar Producers' Association," and representatives added to the Executive Committee to cover all areas.

The Executive Committee now comprises a representative from each of the following firms :—Clay Cross Co., Ltd. ; Constables Quarries, Ltd. ; Wm. Smith (Fluorspar), Ltd. ; Ernest Hinchliffe, Ltd. ; R. C. Conway ; Blanchland Fluorspar Mines, Ltd. ; Weardale Lead Co., Ltd. ; Horace Taylor ; Messrs. James Wilkinson and Sons, Ltd. (Glebe Mine). Chairman, Frederick Franks ; deputy-chairman, Charles A. Jones ; secretary, H. Hebblethwaite, A.C., Chartered Accountant, 5-6, Huttons Buildings, West Street, Sheffield.

Factors Influencing the Moisture Content of Furnace Atmospheres

By F. Gilbert and E. Scheuer

There are a number of sources from which this moisture content may be derived, but in this work the authors direct particular attention to the hydrogen and water content of the fuel and air used for combustion. Graphs have been prepared which give quickly, and with reasonable approximation, the water content of the combustion gases, if the water and hydrogen content of fuel and combustion air are known.

THE work described in this report was primarily devised to obtain an approximate picture of the water content of the burnt gases from the various fuels used for the melting of aluminium alloys in furnaces in which the metal is in contact with the flame and its gases. Any water vapour in contact with the molten metal reacts to form aluminium oxide and hydrogen, the latter being readily soluble in molten aluminium, giving rise to porous castings, and consequent lowering of mechanical properties, leakage under pressure, and, in the case of forgings and sheets, causing blisters after heat-treatment. Water vapour is therefore considered to be as deleterious to the metal as free hydrogen. Some authorities ascribe an even greater danger from water vapour than from hydrogen gas, as the hydrogen resulting from the reaction is in an atomic form, and more readily absorbed by the aluminium.

The conclusions given may be of interest to readers working with metals other than aluminium, as water vapour is often an undesirable constituent of the atmosphere of furnaces used for the melting and heat-treatment of many metals—e.g., copper.

The moisture in a furnace atmosphere can be derived from four sources, these being (1) the air used for combustion; (2) the fuel; (3) the refractories; (4) the raw material charged. This paper deals with the first two sources only, as the others are more easily controlled by the choice of suitable refractories, pre-treatment of the furnace lining, and by the drying of the raw materials before charging.

The moisture derived from the air and fuel will be considered under three headings :—

(1) Moisture in the air used for combustion.
(2) Moisture in the fuel.
(3) Hydrogen in the fuel.

Typical calculations for these three sources are appended, using a case of practical interest as an example, and from these calculations graphs have been derived from which the total moisture content of the burnt gases can be readily ascertained. The graphs do not make any provision for either excess air, which is probably present to a small degree, nor for incomplete combustion, which, in any case, should not occur in an efficiently run furnace. We are of the opinion that these deviations from the assumed ideal combustion are not sufficiently great to warrant the complications necessary in providing for them.

Some tables have also been calculated which give interesting information on the relative importance of the various sources of moisture in furnace gases when
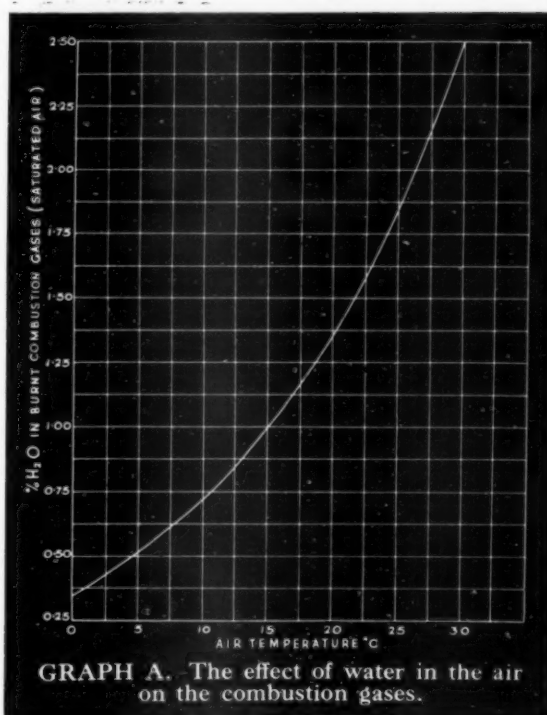
GRAPH A. The effect of water in the air on the combustion gases.

using various fuels, and working under two sets of atmospheric conditions which could be considered as the extreme ends of the range of moisture encountered in practice. The figures given are the percentage by weight of water vapour in the gases after complete combustion of all carbon and hydrogen into CO_2 and H_2O.

Calculation of the Graphs

Graph A.—This shows the relationship between the air temperature and the weight percentage of water vapour in the combustion gases, using dry carbon, and air of 100% humidity.

Assume that the air used for combustion is at 15° C., humidity 75%. Saturated air at 10° C. contains 1·07% H_2O, 75% saturated 0·80% H_2O. For complete combustion, 100 lb. carbon require 1,160 lb. of dry air, and 1,170 lb. of air at 15° C., 75% humidity, which would contain 9·35 lb. H_2O.

GRAPH B. The effect of moisture in the fuel on the combustion gases.
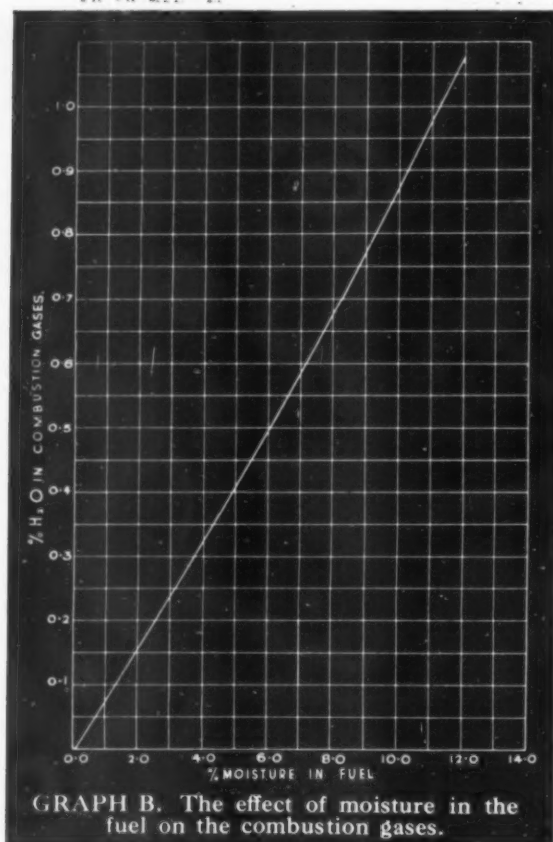
The weight of the burnt gases would be 1,270 lb. (weight of air plus weight of fuel), and contain 9·35 lb. $H_2O = 0·74\%$. From a series or similar calculations Graph A was derived, giving figures for saturated air from 0°–30° C. As the figures given by this graph are the percentages of moisture obtained by using saturated air, it is essential that they be reduced in ratio to the percentage humidity of the air.

Graph B.—The relationship between the weight percentage of moisture in the fuel and the weight percentage of water vapour in the combustion gases.

Assume that a fuel (coke) contains 2·5% moisture, the balance being carbon, 100 lb. dry carbon require 1,160 lb. air, 100 lb. at 2·5% moisture require 1,131 lb. The waste gases weight 1,231 lb. (air plus fuel) and contain 2·5 lb. of moisture = 0·20%. Similar calculations gave Graph B, showing the effect of 0–12% moisture in the fuel.

Graph C.—This shows the relationship between the weight percentage of hydrogen in the fuel and the weight percentage of water vapour in the combustion gases, using dry air and fuel. (Fuel assumed to be carbon and hydrogen only.)

Assume that a fuel—e.g., creosote pitch—contains 6% hydrogen, balance carbon. When 100 lb. are burnt, 6 lb. of hydrogen require 207 lb. of air, and 94 lb. of carbon 1,090 lb. of air. The total air required is 1,297 lb., the waste gases weight 1,397 lb. (air plus fuel), and contain 54 lb. of water derived from the hydrogen = 3·86%.

From similar calculations Graph C was made, showing the percentage of water in the waste gases, using fuel containing 2–14% of hydrogen.

To use the above graphs, all that is necessary is to make an addition of the percentages of water vapour obtained for each source. An example to illustrate this is given below.

Creosote pitch containing 6% moisture and 6·5% hydrogen is burnt with air at 17° C., 50% humidity.

From		%
Graph A	Saturated air at 17° C. = 1·12%, 50% saturated	= 0·56
Graph B	Moisture in fuel—1%	= 0·08
Graph C	Hydrogen in fuel—6·5%	= 4·18
	Moisture in waste gases	4·82
	Calculated value	4·81

Owing to the fact that Graph A is plotted on the assumption that dry fuel is used, and Graph B and C that dry air is used for combustion, the figures obtained are not absolutely correct. Nevertheless, on checking against calculated figures for the widest possible ranges of water and hydrogen content, they show an accuracy of ± 0·02%.

Graph D.—This shows the adjustment to be applied to the hydrogen percentage, when a fuel contains appreciable amounts of constituents other than carbon and hydrogen.

The foregoing graphs were primarily devised for assessing the amounts of moisture given by fuel oils and pitches, which contain such small amounts of impurities that no allowance for them was necessary, and for cokes whose hydrogen content is small.

Should they be used for coals, which contain up to 20% of materials other than carbon and hydrogen, to ignore these impurities can lead to an appreciable minus error. In such a case, to find the amount of moisture supplied to the combustion gases by the hydrogen of the fuel, it is essential that the amount of hydrogen in the fuel be expressed as a percentage of the total of the carbon plus hydrogen, and that this adjusted figure be read on Graph C. For this purpose, Graph D was made, giving the adjustment necessary to obtain a corrected figure. The figure for impurities is found (for reasons explained below) by subtracting from 100% the total percentage of C + H_2 given in the analysis of the fuel. The line representing this figure for impurities is taken (or interpolated) on the graph, the corrected figure for the hydrogen percentage being found by plotting a vertical line from the uncorrected hydrogen percentage on the abscissa, up to the intersection with the impurities line. A horizontal line from the point of intersection to the left-hand scale gives the corrected figure to be read on Graph C. An example of the use of Graph D in conjunction with Graphs A, B and C is given below.

Coal burnt with air at 20° C., 75% humidity.

Analysis of coal : H_2O, 5% of wet material ; C, 85% of dry material ; H_2, 5% of dry material.

Impurities : 10% (ash, N_2, S, O_2, etc.) of dry material.

		%
Graph A	Moisture in combustion gases for saturated air at 17° C. = 1·35%	
	For air, 75% ; humidity 1·35% = 75%	1·01
Graph B	Moisture in combustion gases for 5% H_2O in fuel	0·41
Graph D	5% H_2, 10% impurities = 5·60% H_2 corrected figure.	
Graph C	Moisture for 5·60% H_2 in fuel	3·60
	Moisture in furnace gases	5·02
	Calculated value	4·99

On checking values obtained from the use of Graphs A, B, C and D in conjunction, against correctly calculated values for a wide range of coals and air conditions, they were found to have an accuracy of $\pm 0.05\%$.

No pretensions to strict mathematical and theoretical accuracy are claimed for this method, as there are too many interfering elements to be taken into consideration.

Classification of Impurities

Some explanation is necessary for the classification as impurities of all the constituents of a fuel excepting the carbon and hydrogen. The ultimate analysis of coal is usually expressed as the percentages of carbon, hydrogen, ash, sulphur, nitrogen, and " O_2 plus errors " in the dried material. We treat the sulphur, nitrogen, oxygen, etc., as though they were ash, and did not contribute to the amount of the gas produced in combustion. In practice, the role played by these constituents is assumed to be as follows :—

   (i) Sulphur, excepting that present as sulphates, will produce SO_2 (using about its own weight again of oxygen) and increase the total of gas by five times the weight of oxygen used plus the weight of the sulphur (i.e., about six times the weight of the sulphur).

  (ii) Nitrogen will increase the total by its own weight only.

 (iii) Oxygen will decrease the quantity of gas by the weight of the air it replaces—that is, by five times the weight of the oxygen.

All these assumptions are only approximations, and as regards (iii) even the analysis figure is uncertain, being found by difference. From calculated figures for typical coals, we find that the errors introduced by treating these constituents as though they were inert are of small magnitude. On the other hand, to provide for them individually would lead to many complications, with very little increase in the accuracy of the final figure.

A small error is introduced by the fact that the moisture in coal is given as a percentage of the moist material, whilst the carbon and hydrogen are given on the dried material. We have calculated representative cases, and are satisfied that the error in the moisture content of the combustion gases amounts to only a few hundredths of 1%.

Survey of Typical Cases

Table I is appended to give some comparison of the factors influencing the amount of moisture in a furnace atmosphere when using typical solid, liquid, and gaseous fuels. The figures given for producer and coal gas were not derived from the graphs, and were calculated on the assumption that the gases were dry. The usual metallurgical practice is to burn producer gas without previous washing. Should the gas be washed in a wet coke scrubber, or similar apparatus, an approximate figure for the water vapour thus introduced into the combustion gases can be obtained by dividing the percentage of moisture in the producer gas by two (as one volume of producer gas needs approximately 1 volume of air).

GRAPH D. Adjustment for impurities in the fuel.
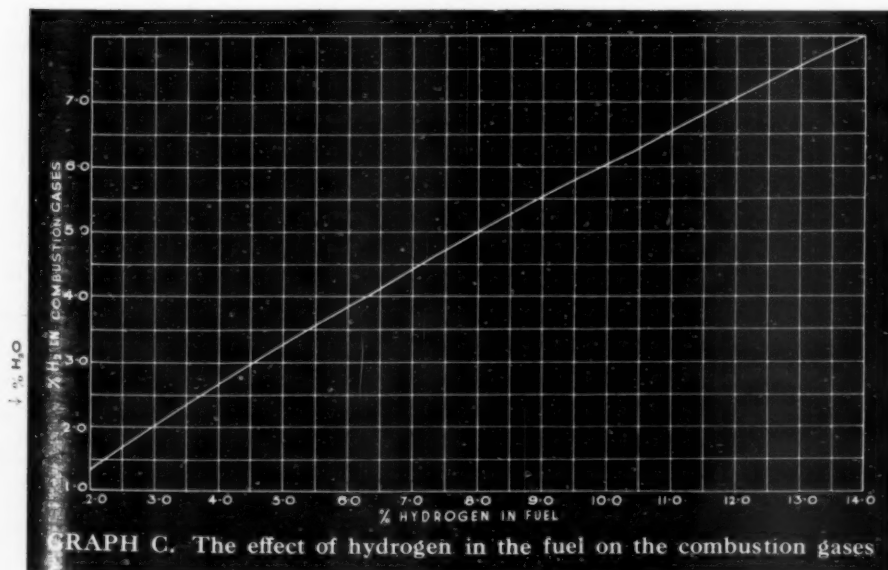
GRAPH C. The effect of hydrogen in the fuel on the combustion gases

TABLE I.
THE FACTORS INFLUENCING THE AMOUNT OF MOISTURE IN A FURNACE ATMOSPHERE.

Fuel.				Contribution to Moisture in Furnace Gases.							
Type.	Moisture, %.	Hydrogen, %.	Impurities, %.	Dry Winter Conditions. Air at 0° C., 50% Saturated.				Damp Summer Conditions. Air at 25° C., 100% Saturated.			
				Moisture.	H$_2$.	Air.	Total.	Moisture.	H$_2$.	Air.	Total.
Coke	2·5	0·5	2·0	0·20	0·33	0·17	0·70	0·20	0·33	1·85	2·38
Anthracite	1·0	3·5	4·0	0·08	2·30	0·17	2·55	0·08	2·30	1·85	4·23
Steam coal	5·0	4·3	4·2	0·41	2·95	0·17	3·53	0·41	2·95	1·85	5·21
Coking coal	7·0	5·4	10·0	0·59	3·86	0·17	4·62	0·59	3·86	1·85	6·30
Creosote pitch ...	1·0	6·0	1·0	0·08	3·88	0·17	4·13	0·08	3·88	1·85	5·81
Heavy oil	0·2	8·5	1·0	0·01	5·26	0·17	5·44	0·01	5·26	1·85	7·12
Producer gas	—	0·94	—°	—	3·96	0·10	4·06	—	3·96	1·06	5·02
Coal gas	—	21·2	—†	—	14·20	0·17	14·37	—	14·20	1·86	16·06

° Analysis of Producer Gas:—CO$_2$, 8·4%; CO, 31·4%; H$_2$, 0·86%; "CH$_4$" 0·34%; N$_2$, 59·0%.
† Analysis of Coal Gas:—O$_2$, 1·11%; CO$_2$, 7·65%; C$_2$H$_5$, 11·05%; CO, 19·5%; H$_2$, 9·14%; CH$_4$, 41·8%; N$_2$, 9·75%.
All the figures are percentages by weight.

Similarly, an approximate figure for coal gas is obtained by dividing the percentage of moisture in the gas by 12. That is, if a coal gas was saturated at 25° C.—i.e., its dew-point was 25° C.—the amount of moisture in the burnt gases would be increased by 0·4%, which is small in comparison to the moisture obtained from the hydrogen and its compounds.

Conclusions

The three sources of moisture, in normal combustion conditions, have the following order of importance.
(i) The hydrogen content of the fuel.
(ii) The moisture content of the air used for combustion.
(iii) The moisture content of the fuel.
The most marked influence on the water content of the furnace atmosphere is the hydrogen content of the fuel. If the hydrogen is more than 5% it is the predominating source of moisture, and no changes in either the moisture in the air, or moisture in the fuel have any considerable effect on the final moisture content of the combustion gases.

Under normal conditions, the moisture of the air has a small effect as compared with the hydrogen of the fuel. With very moist air, the moisture of the air contributes to the total moisture of the combustion gases an amount of the same order of magnitude as the hydrogen content of most fuels.

The moisture of the fuel itself plays a significant part only if the atmospheric moisture and the hydrogen content of the fuel, are low. For example, dry-quenched coke (1·0% moisture) would yield a furnace atmosphere with only half the moisture content given by water-quenched coke (5% water) in very dry weather conditions. For all fuels with a hydrogen content above 3%, the moisture of the fuel has an insignificant effect compared with the effect of the hydrogen.

Two Years of Fuel Efficiency

A brief summary of the progress that has been made in the fuel efficiency campaign since July, 1942, is given in booklet recently issued by the Ministry of Fuel and Power. This period has seen the formation of Fuel Efficiency Committees in each of the twelve Civil Defence Regions, and the planning and carrying out of a systematic drive for fuel efficiency throughout the industries of the country under the direction of the Ministry's main Committee, of which Dr. E. S. Grumell, C.B.E., is chairman.

The central feature of the campaign has been factory inspection. Seven hundred engineers, both full-time and voluntary, have been enlisted and are carrying out inspections at factories at the rate of over 1,500 a month. Up to December, 1943, nearly 12,000 first visits and 5,000 follow-up visits have been made to factories whose coal consumption aggregates nearly 40,000,000 tons per annum. In several of the Regions every coal consumer of any size has been visited once, or oftener. The work is under the direction of the Regional Committees, who scrutinise the reports and contribute their experience in the recommendations made.

Many trade associations have formed their own Fuel Efficiency Committees, whose work has been co-ordinated with that of the Ministry. In the case of the major fuel-using industries—gas, electricity, coke-ovens, railways, collieries, iron and steel, etc.—with whom fuel efficiency has always been a major preoccupation, joint meetings have been held with the Ministry's Committee and full co-operation has been maintained. One development in particular has been fostered—namely, that whereby practical help is given to the smaller units of industry by the officers of the larger units. Such a system has been organised by the gas industry, among others.

Another important branch of the Ministry's work has been on the technical and educational side. Some 30 technical bulletins have been issued and widely distributed, and these, while supplementing the work of visiting engineers, remain as a permanent source of technical assistance on fuel efficiency problems. The aggregate distribution of these bulletins has now reached a figure of 800,000.

For the benefit of managements, stokers and factory personnel, training schemes have been established in every centre, and illustrated lectures and demonstrations have been given to over 14,000. These courses have been operated at 120 centres, many of which have asked for repeat courses in the same or other subjects. A later development has been specialised lectures on various aspects of power and heat utilisation adapted to the needs of the particular region.

These and many other developments are summarised in this pamphlet. Behind its facts and figures lies the story of an enormous expansion of fuel efficiency activities, without which the country's industries would have found it difficult to maintain war production with the fuel supplies available.

Malleable Cast Iron
Part III.—Production Aspects
By J. A. Wylde

In this part of the series of articles the author discusses the more important aspects of production and emphasises the need of the provision and maintenance of first-class patterns and moulding equipment. Moulding and core sands are briefly discussed, and various melting processes are summarised, attention being especially directed to air- and open-hearth furnace processes. The annealing of whiteheart and blackheart malleable iron castings is briefly described.

A S this subject is a very extensive one, its various phases can only be dealt with briefly in the space at the writer's disposal. In order to keep this section within reasonable limits, it is assumed that the reader is conversant with general foundry practice, attention, therefore, will be mainly focused upon the peculiarities of malleable cast iron production and the processes which do not occur in the manufacture of grey cast iron. Blackheart and whiteheart procedure has many things in common, and, in view of this, both materials will be dealt with together.

Pattern Equipment

The first essential to ensure good clean castings, true to dimension, is the provision and maintenance of first-class patterns and moulding equipment. Many users of castings adopt a very short-sighted policy, looking upon patterns as a necessary evil. Saving a few shillings by providing cheap pattern equipment may mean a good deal of expenditure in time and labour in machining and assembling the final product.

For short runs liable to repeat, good wooden patterns of well-seasoned mahogany are to be recommended. For running jobs it is advisable to have brass working patterns and mahogany coreboxes reinforced with brass on wearing faces, and, if the quantity permits, iron or steel coreboxes. When metal pattern equipment is being produced, pine master patterns will suffice. All discerning users of castings, providing their own patterns, invariably consult the casting supplier on the manner in which the patterns are to be made. Every foundry has its own peculiarities and, in addition, the foundryman can often bring to the designer's notice points about the design for a casting which are not in keeping with good foundry practice, and can suggest modifications to facilitate the making of a sound product.

As a general guide, the contraction for wood-working patterns is 1 in 96, and for wood master patterns 1 in 48. On the question of contraction the foundryman should always be consulted, as with malleable production this is liable to vary with the nature of the job. Contraction takes place during cooling, but a variable expansion takes place during annealing.

Owing to the high rate of contraction in malleable castings, the pouring gates should be designed as feeders and require to be as near the main body of the casting as practical conditions permit. In the case of large castings, spinning gates or filter cores should be provided to prevent, as far as possible, any undesirable elements entering the mould. Additional feeders are essential when casting heavy sections to ensure homogeneity.

An external view of a modern type malleable foundry showing part of the pulveriser house and furnace stacks.

Chills are also introduced to accelerate cooling and to counteract pre-graphitisation.

The casting designer can be of real assistance to the founder by keeping an even balance between sections and introducing good radii where abrupt section changes are unavoidable. A nice even flow of metal is desirous, so that the crystalline formation can proceed in an orderly fashion. The chief causes of weakness in malleable cast iron are shrinkage and sponginess generally due to sudden changes in section, but most difficulties of this nature can be overcome with correct foundry supervision.

Much experimental work is necessary before a pattern is put into production. Trial castings are usually made to prove that the method of gating and feeding ensures the casting being sound at every point. With the more extensive use of X-ray apparatus in foundry laboratories, no doubt in time the work involved in the production of castings will be greatly simplified.

Moulding and Core Sands

Sand, up to the present time, has proved the most suitable material for producing moulds to receive metal cast at high temperatures. Other materials have been tried, but no suitable substitute has yet been found for use in the malleable cast-iron industry. Silica and alumina are the two chief constituents required in a ratio of approximately 9 to 1 respectively.

The sand should be as free as possible from impurities,
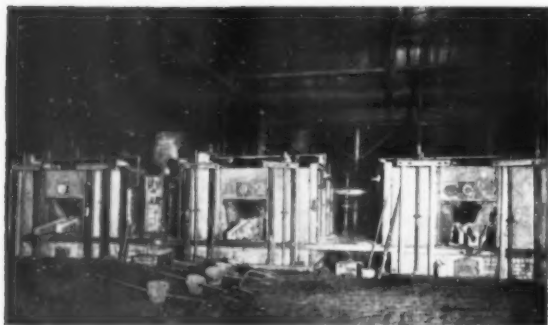
Preheated forehearths for pro-
ducing malleable cast iron from
the cupola.

such as manganese, iron oxide and
lime. There are two main impurities
to guard against—iron oxide, which,
if in excess, makes the sand fusible,
and carbonate of lime which gives
off CO_2 under the action of heat.
This is liable to cause parts of the
mould to collapse and to cause
" scabbing " and irregular surfaces.

Deposits of suitable moulding sand
are, fortunately, within easy reach
of most foundries in this country.
Good foundry sand is found in
deposits of glacial origin, the silica
grain being formed from granite
quartz.

The ideal malleable foundry sand
requires nicely rounded silica grains
of even size with a sufficient coating
of alumina or clay to give a satis-
factory bond and still be sufficiently
porous to allow the gases to escape.
Small grains and an excess of clay tend to clog the mould
face and trap the gases within the mould. Briefly, the
main physical properties of good malleable foundry sand
are refractoriness, bonding strength, and, above all,
porosity. Malleable castings are made in " green sand "
moulds—that is, in the moist, undried condition.

In moulding large castings, freshly mixed " facing "
sand is rammed against the face of the pattern, and the
mould finished off with " backing " sand taken from the
floor. The ordinary " green " sand in its natural con-
dition would fuse if used in making a large slow-cooling
casting. This would cause " scabbing " on the face of the
casting. To avoid this, a percentage of coal dust or some
proprietary composition is mixed with the facing sand.
The action of the coal dust particles is to generate gases
when heated, which form a protective film over the face
of the mould, preventing the metal penetrating the sand.
In the case of small castings which are quick cooling,
this precaution is not so essential.

Foundry managers are devoting increasing attention
to sand control, and the writer has witnessed examples of
considerable reductions in foundry losses due to an
intelligent approach to this problem.

Moulding sand requires to be tested regularly for
permeability, green strength, grain size, and moisture
content. An open sand is essential to enable the gases
to get away freely.

Core sand offers a different problem to moulding sand.
Sea sand, or silica sand, is most desirable, but the
bonding is artificial, being provided by a linseed oil or
cereal base. The sand requires to be mixed mechanically
to ensure the grains being thoroughly coated. As in the
case of moulding sand, the mixture must be porous, but
able to withstand the flush of molten metal after drying.

Drying must be carefully controlled. If the cores are
burnt or are hard, they may be too strong and resist
contraction of the metal, causing cracking of the castings
during cooling. Cores should be baked in ovens with the
temperature thermostatically controlled.

An enlarged view of one of the forehearths.

Regular laboratory tests require to be carried out on
core sand as in the case of moulding sand.

Melting Processes

Crucible Process.—Melting is carried out in a natural
or forced draught pot furnace. The fuel used is low-
sulphur coke, and the metal is melted in plumbago
crucibles, holding about 56 lb. of metal. This process
has distinct advantages over others, as the metal does
not come into contact with the fuel, and the chemical
constituents can be easily controlled.

Crucible melting was generally confined to the pro-
duction of small whiteheart castings. As production is
slow and fuel costs are high, this form of melting is not
extensively used to-day. At one time Government
departments and certain authorities specified " Crucible
Malleable," but the process is now slowly becoming
obsolete.

Cupola Process.—This is the cheapest and most rapid
form of melting. Due to its inconsistencies, cupola
melting is generally confined to whiteheart production,
where control is not so important.

Malleable cupola practice is similar to grey iron,
except that a higher fuel ratio is necessary. This is
required owing to melting at a higher temperature. In
melting white iron, the silicon, carbon and phosphorous

contents are all lower than in grey iron, hence the necessity for a higher fuel ratio.

Limestone is charged in greater quantities than in grey iron practice, it having two duties to perform. First, it is required to flux away non-metallic impurities, and secondly, to keep down sulphur by forming calcium sulphide which passes into the slag. Under normal conditions melting losses are small, silicon about $0 \cdot 15$ to $0 \cdot 20$, but carbon tends to increase, due to "pick-up" from the fuel, and similarly in the case of sulphur.

It is not unusual, during melting, for part of the charge to become wedged, causing a scaffold. This condition brings about over-oxidation of the metal, and melting losses increase considerably. There is a fall in silicon, manganese and carbon, together with a decrease in temperature. If these "hold-ups" are not dealt with promptly, the metal produced will be useless.

It is due to the possibility of scaffolding occurring and fuel contamination that makes cupola melting an undesirable medium for blackheart production, but by careful melting supervision, manganese adjustment, and the introduction of a pre-heated receiver or forehearth for thoroughly mixing the molten metal passing from the cupola, a good commercial blackheart malleable can be produced. Cupola production is economical from an actual melting point of view, but annealing costs are increased. The percentage yield of good castings is generally lower than are obtained by other processes.

Air Furnace Process.—This is one of the most popular processes used in blackheart production. The furnace is generally fired by coal with natural or forced draught, and for this reason the metal cannot be entirely free from sulphur contamination. It is a slower melting unit than the cupola and is more expensive in the use of fuel. The higher production cost is more than cut-weighed by the improved quality of the castings.

As the charge comes in contact with the flame, similar to cupola melting, there is bound to be a fall in silicon and manganese, together with an increase in sulphur picked up from the fuel. There is a great tendency towards oxidation on the surface of the bath, where the metal is much hotter than lower down at the tapholes. With this method of melting "hard taps" are frequent, and can be very disastrous.

Due to the varying temperatures in the bath, it is usual to have two or three tapholes at varying heights. The top metal, which is hottest, should be used for casting light thin sections. Heavy castings should be poured towards the end of the melt as the lower metal has increased in temperature, and the silicon content reduced by oxidation.

Metal tests are taken in the form of a tapered test-piece about 12 in. long. The sample is taken in a spoon from the bottom of the bath and cooled quickly. The sample, when cool, is broken up and the fractures at various points indicate the suitability of the metal for different types of castings. One of the chief dangers to guard against is oxidation, which commences before the metal reaches the liquid state. When the metal becomes molten it should be thoroughly mixed or "rabbled." Further oxidation takes place when the metal is molten, resulting in the formation of a slag. The slag serves to protect the metal from the flame, but has an oxidising effect on the silicon and manganese in the metal below. This chemical reaction increases the temperature, causing the metal to "boil." The slag is then removed, causing another increase in temperature, followed by a further

slag formation. When the bath sample gives a white fracture, the metal should be tapped immediately. If the skin of the sample is pitted, this indicates that the metal is overheated. Under these circumstances, a small quantity of ferro-silicon should be rabbled into the bath. With good melting control, the addition of ferro-silicon should not be necessary, but this is sometimes unavoidable. "Rabbling" is a most important feature of the process and must on no account be neglected.

The chief objection to the air-furnace melting is the oxidation which takes place during the "tapping-out" period causing some lack of uniformity in the castings produced.

Open-hearth Process.—The open-hearth process is most suitable for a large output, and has found much favour with blackheart producers. It is capable of producing a large tonnage of good quality castings. In this respect it is more economical than the air-furnace.

Melting losses occur due to oxidation of silicon, carbon and manganese, as with the air furnace. Melting losses are similar and must be catered for in the charge. Usually open-hearth furnaces are fired with producer gas, but very satisfactory results are obtained from pulverised fuel used in open-hearth type furnaces. Furnaces using producer gas are fitted with regenerative chambers, making melting more economical. To be really economical, however, the furnaces should be worked continuously.

As in the case of the air furnace, the metal should be tapped as soon as the metallurgist approves the bath sample. It is usual to test for carbon and fracture prior to tapping out. There should be a minimum of delay in getting the metal away, and on no account should it be held or there will be a fall in silicon tending to make the metal sluggish. To expedite handling, it is usual for the metal to be taken off in crane ladles and redistributed in small hand ladles. To remove the whole of the metal from the spout in small ladles is a slow process, but some foundries prefer to remove all metal in this manner. It is considered the loss of temperature which takes place in double handling is more detrimental than the change in analysis which may take place due to oxidation of the surface metal while tapping is in progress. With a new furnace it is most essential that it should be thoroughly dried, and a furnace in use should not be allowed to cool down between melts. In melting, small scrap should be charged first, forming a bath to receive the pig. The pig is immersed in the molten scrap and is protected from undue oxidation. Charging should be done evenly, as the piling of material tends to cause a baffle for the flame and irregular melting. It is important that any masses of metal are broken up to facilitate melting. When all the charge is melted a flux is added to thin out the slag, which is raked off through the rear doors of the furnace.

"Rabbling," as in air-furnace practice, is a very essential part of the open-hearth process. There is the same tendency of surface oxidation and lowering temperature towards the bottom of the bath. This is counteracted, to some extent, by "rabbling," which mixes up the molten metal to maintain a fairly even temperature throughout.

Tap-holes may be situated at varying heights to enable the top metal to be drawn off first. The main advantages of the open-hearth over air-furnace practice are quicker melting, higher melting temperature, and

A " Beehive " type annealing oven being charged
with castings for annealing.

A " Beehive " annealing oven with
the " wicket " broken down prior to
the discharge of annealed castings.

cleaner metal. These advantages assist in producing
castings of consistent quality.

In addition to the melting plants described, rotary
and electric furnaces find a certain amount of favour.
They are not particularly suited to producing a large
tonnage of metal, although the castings are of a high
quality. The electric furnace is more popular in America,
and will, no doubt, be the malleable melting unit of the
future, when production costs can be reduced to a more
economic level. Duplex and triplex processes are used
in America and in this country, utilising cupola, con-
verter and electric furnaces at different stages of the
process.

When the castings have been poured they are generally
left to cool in the moulds. After the castings have cooled,
gates and feeders are removed. They are sand-blasted,
or barrelled to remove the adhering sand, cores and
wires. Subsequently, the castings should be carefully
inspected for faults and gauged, if necessary, and then
passed to the annealing department.

Annealing Process

The ovens are generally of the batch type, being
round, rectangular or square. They are built of insulating
bricks and are generally fired by coal, gas, oil or pul-
verised fuel. Continuous ovens are being developed and
offer distinct advantages over the batch type. They
greatly facilitate the handling of castings in a systematic
manner, and will find increasing favour with malleable
founders in the future.

During this war long kiln ovens, used for brick-making,
have been adapted successfully, but, due to their size,
are only economic for large production. Small electrical
units are also in use, but at present this is an expensive
method of annealing. The electric oven is extremely
useful for experimental work, and for annealing small
batches required for special service.

The castings are packed in annealing cans or pots
made of a low-grade cast iron which will not graphitise.
These cans vary in size, averaging from 12 in. to 36 in.
diameter or square, and generally 1½ in. to 2 in. thick.

The cans are made in rings or squares without tops or
bottoms. Opinion in regard to shape is divided. Some
favour the square type can as a maximum packing space
is obtained. Others prefer the round type for two good
reasons—namely, distortion in a round can is less liable
and the heat will circulate more readily between stacks
of round cans. In packing, the cans are mounted in
stacks, the first can being placed on a cast-iron stool.

Packing Whiteheart Castings.—The castings are packed
in red hæmatite ore, broken down to the size of gravel.
The new ore is rich in oxygen and should be mixed with
a percentage of used or " blue " ore. The castings
should be packed at least 1 in. from the sides of the can
and should be well supported. Iron rods are generally
used for tamping down the packing material and the
cans are hammered and shaken as the stack increases
in height. One of the most important points in packing
is to ensure the castings are well supported and that
there are no cavities.

The normal height of a stack is between 5 ft. and 6 ft.
When the stack is completed a lid is placed on the top
can and all joints are luted with a mixture of black
sand and fire-clay. After all the stacks in an oven are
completed, the wicket is bricked up and luted ; firing
is then commenced.

The packing of castings requires considerable skill and
experience, as various types of castings require different
packing conditions. An experienced packer can reduce
troubles of distortion and expansion by careful arrange-
ment of the castings in the cans.

Packing Blackheart Castings.—There is little difference
between blackheart and whiteheart annealing practice
apart from packing material, temperatures and firing
periods. As an oxidising action is not required, the
castings can be packed in any chemically inert material,
such as black sand, mill scale or crushed slag. It is most
important that the castings should be well supported
by packing material to prevent undue distortion.

Providing the castings are protected from the actual
flame, blackheart castings could be annealed without
packing material were it not for the possibility of

distortion. Attempts have been made to anneal without packing by introducing a lid between each can. This method brings about jointing troubles as the intermediate packing lids distort easily. Although the castings are relieved of the weight above by the intermediate lids, there is a tendency for them to distort under their own weight. The action of the two annealing processes has already been described.*

When the oven cools the wicket is knocked down and the stacks of cans are " dropped." The annealed castings are separated from the ore, or packing material, and passed to the fettling department, where gates, fins and rough spots are removed by grinding and dressing with hand tools or pneumatic chisels.

Other operations are sometimes necessary, such as drifting cored holes, correcting distortion and setting to gauges. After the castings are ground, dressed and

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* METALLURGIA, July 1, 1944, p. 124.

straightened, they are finally shot-blasted, or barrelled, to remove the adhering sand prior to despatch.

ERRATA

IN the article by Mr. J. A. Wylde on " Malleable Cast Iron," in the July issue, the following corrections should be made :—

At the foot of the first column on page 124 the effect of oxidation should be expressed as—

$$3Fe_2O_3 + Fe_3C = CO + 2Fe_3O_4 + 3Fe$$
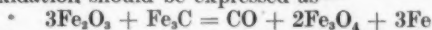
On the same page, second column, fifth line of text from top, substitute the word " mainly " for the word " still." On page 129, in the table at the bottom of the first column, the bend test for whiteheart should read " 45° on 2 in. dia. bar " ; and for blackheart, " 90° on 2 in. dia. bar." On the same page, second column, seventh line down, substitute an elongation of " 14 to 18% " for " 10 to 14%."

The Protective Influence of Manganese in the Corrosion of Aluminium-Containing Magnesium Alloys

By F. A. Fox, M.Sc., and C. J. Rushrod, M.Sc.
(Magnesium Elektron, Ltd.)

Recent American investigations have indicated that high-purity magnesium-base alloys (particularly those of low iron content) are much more resistant to the attack of sodium chloride solution than are commercial alloys of normal purity. As a result of an investigation described in a recent paper,* it is shown that the presence of an amount of manganese in excess of a certain critical limit is able to offset the accelerating influence of iron contamination on the corrosion rate of these alloys. The work is briefly described here, and the authors' conclusions given.

RECENT American investigations of the corrosion of magnesium and its alloys has indicated that one of the predominating influences in producing reduced corrosion resistance is the presence of an iron content exceeding a limiting small amount.[1, 2] Hanawalt and his collaborators state that iron when present in quantities which exceed about $0·017\%$ in pure magnesium, and about $0·002\%$ in the aluminium-containing alloys, leads to enhanced attack in salt water. This has led to considerable stress being laid on the elimination of iron from magnesium alloys which are to have a good corrosion resistance.[3, 4]

The desire to reduce the iron content of standard magnesium alloys has already led to the formulation by the A.S.T.M.[5] of specifications calling for low iron maxima. It is noteworthy that the maxima called for in these specifications are $0·005\%$, and an alloy on the upper limit of these specifications is consequently outside the most rigorous limits laid down by Hanawalt, Nelson and Peloubet.[1]

The modifying influence of manganese on the corrosion behaviour of the aluminium-containing alloys does not, however, seem to have been adequately studied in relation to these effects of iron. Since the commercial alloys, in Europe at least, have since about 1928 contained manganese of the order of about $0·3\%$ as an essential alloying addition, and since the aluminium-

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* J. Inst. Metals, July, 1944, pp. 325–338.

containing alloys used in the American work did not same time as a $0·3\%$ manganese addition, it was felt that work on the influence of manganese should be undertaken as a first step in the further elucidation of the relation between the effects of iron and manganese. In other words, it was felt desirable to make some quantitative estimate of the influence of manganese on the corrosion-resistance of aluminium-containing alloys which carry a " normal " iron content of about $0·02–0·03\%$ with some work to cover iron contents slightly higher than this. These results were then to be compared with results obtained from higher purity materials of otherwise similar composition.

Apart from some reference in the work already quoted, the influence of manganese on magnesium is already known in a general way, and was investigated by Kroenig[6] and collaborators. The corrosion behaviour of alloys of the magnesium-aluminium-manganese system was also examined by Boyer.[7] These latter investigators, however, took no cognisance of the iron content of their alloys, and their results must now be regarded as incomplete.

General Experimental Details

It was desired to work with alloys the essential composition of which was near those used in this country as standard alloys ; it was decided, therefore, to investigate the behaviour of two alloy types falling within a

apparently carry the "normal" iron contents at the range of aluminium contents between about 4 and 8%. The alloys chosen for this exploration were those conforming chemically to the requirements of the specifications D.T.D. 325 and D.T.D. 59A. It was decided in the first instance to examine these alloys in the chill-cast state, using as raw materials castings consisting of bars generally similar in form to the D.T.D. type of sand-cast bar, cast in an iron mould. The influence of manganese on the corrosion resistance of alloys of this kind (in one case with varying iron content) was tested by immersion in 3% sodium chloride solution and also, for confirmation, by atmospheric exposure tests on one alloy (D.T.D. 325). This latter check was regarded as important in relating the arbitrary immersion test to results more nearly resembling those which would be obtained under service conditions for the unprotected metal.

The use of sodium chloride immersion tests has been widely accepted as a standard for the corrosion testing of magnesium alloys,[8] and 3% was selected as a concentration near that in sea water, and also as being one in common use in this country and elsewhere. Our own previous work has, however, shown it to be necessary that, to avoid anomalous results with a new corroding bath, the solution should be buffered by the addition of a small quantity of magnesium oxide, which immediately establishes a pH of about 10·2; this was done in all cases in the tests described.

Conclusions and Discussion

The results of the experiments described in the paper leads to the following conclusions :—

(1) For chill-cast alloys containing about 5% or about 8% aluminium the presence of manganese in quantities of the order of about 0·3% is sufficient to offset the harmful effects of about 0·02–0·03% iron when tested by immersion in 3% sodium chloride solution.

(2) In the chill-cast state an alloy containing about 5% aluminium behaves similarly under atmospheric attack—i.e., the presence of about 0·3% manganese appears to offset the harmful effects of 0·02–0·03% iron. A relation between atmospheric exposure tests and complete immersion tests is thus indicated.

(3) For an alloy containing about 8% aluminium and the "normal" iron content, the corrosive influence of immersion in 3% sodium chloride is greatest for the solution-treated and precipitated state, intermediate for the solution and precipitated state, and least for the chill-cast state. In the two former conditions the presence of 0·4 and 0·3% manganese respectively is required to offset the presence of the iron at least to the extent of producing an asymptotic curve.

(4) With chill-cast alloys containing about 5% aluminium and with lower iron contents (of the order of 0·01 or 0·005%) the corrosion resistance is improved by the addition of increasing quantities of manganese (as judged by immersion tests in 3% sodium chloride solution). The corrosion resistance of the alloys with a very low manganese content is considerably better for the low-iron alloys than for similar low-manganese alloys containing higher iron contents. With manganese contents of more than about 0·2%, however, the high- and low-iron alloys show similar corrosion resistance when tested in this way.

Some points in the above conclusions merit further discussion.

It is interesting to note that in the work of Hanawalt, Nelson and Peloubet,[1] it appears as though the manganese additions were below those required to give the best protection (this is at any rate to be assumed, since frequent reference is made to additions of 0·2% manganese ; full analytical data are not provided). This difference between our own materials and theirs will help to account for the difference in results. The difference in the results is, for example, clearly shown by reference to Fig. 8 of the paper of Hanawalt, Nelson and Peloubet. Here, an alloy containing 5% aluminium is shown as being at the "tolerance limit" only if it contains as little as 0·001% iron. The same alloy with 0·2% manganese must contain as little as 0·002% iron to be at the same tolerance limit. This method of evaluating alloys by the sharply dividing tolerance limit (expressed as less than 0·2 mg.cm.²/day) is perhaps open to criticism in that data are not available to show how much worse alloys just outside the tolerance actually are ; the presentation is analogous to that of a one-contour ordnance survey map.

Another factor which may have an influence is the difference in the type of corrosion tests used.

All corrosion tests are, of course, arbitrary to a greater or lesser extent, and the real test is that of service. However, our own work does at least show one series of experiments in which the metal is subjected to atmospheric attack. This test confirms the general run of the results produced by the immersion in 3% sodium chloride solution.

Our own results, as far as heat-treatment is concerned, agree with the work of Boyer,[7] in so far as he found that "as-cast" magnesium-base aluminium- and manganese-containing alloys were more resistant to salt-water corrosion than was the same material in the fully heat-treated state. Solution treated metal was found by Boyer to possess the least corrosion resistance.

Our own results also agree qualitatively with those of Gann,[5] as far as alloys of normal iron content are concerned. There is, nevertheless, a difference between our results and these in quantitative terms. This was observed in the alloys tested in so far as the ranges quoted there for the corrosion rates of alloys of comparable composition in the solution treated and fully heat-treated conditions are much wider than the corresponding ranges obtained by us generally in these states. Here, again, differences in manganese addition may be responsible.

The work described does not by any means fully explore the position, and it is hoped shortly to publish further data concerning the behaviour of low-iron alloys in the sand- and chill-cast and heat-treated states, when corroded atmospherically and with 3% sodium chloride solution. Work is also proceeding which is aimed at elucidating the part played by iron and manganese in the mechanism of sodium chloride attack on magnesium alloys.

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The American National Emergency Steels

Their Evolution, Present Status and Future

By Roger F. Mather, M.A., S.M., A.I.M.E., A.S.M., S.A.E.

(Chief Metallurgist, Willys-Overland Motors, Inc.)

A comprehensive and detailed account is given of the development of the American National Emergency steels and includes the recent revised list of NE steel compositions. The article has been reviewed by Mr. Charles M. Parker, Secretary of the General Technical Committee of the American Iron and Steel Institute who is a recognised authority on the NE steels, so that the information given can be regarded as entirely reliable. Various aspects of the subject are discussed covering raw materials, steelmaking and application.

AN account of the conservation of ferro-alloys in the United States may well begin in June, 1940, when after a brief interlude the American steel industry resumed the high level of production it has maintained ever since. At that time the output of alloy steel amounted only to about 400,000 tons per month, and considerable stockpiles of ferro-alloys were in existence, so that it was several months before any shortage of alloys was experienced. Any local difficulties in securing sufficient alloy steel for armaments were overcome by a system of priorities, since the tonnage of steel required for the purposes of defence was then about one-tenth of the total quantity produced.

In May, 1941, the American Iron and Steel Institute published its first list of standard steel compositions. The system of classification was basically the same as that adopted by the Society of Automotive Engineers, although there were some significant differences. The list proposed by the Institute included the steels used in such fields as the railroad, construction, shipbuilding, electrical, and petroleum industries, which the then existing S.A.E. list did not attempt to cover. The Institute list contained a total of 60 carbon and 76 alloy steels, which were selected on the basis of 1940 tonnages from the 4,000 different compositions then produced. The compositions selected accounted for 94% of the total tonnage melted in 1940, or, in other words, the 3,800 compositions excluded comprised only 6% on the basis of tonnage. Certain special types of steels were not included in the Institute list, particularly those which are sold under brand names, such as low-alloy, high yield strength steels and nitriding and tool steels. This step towards the standardisation of steels can hardly be called a direct conservation measure, yet it helped to increase production and reduced the number of steels for which substitutes had later to be found. The first joint list of standard steel compositions was published by the Institute and S.A.E. in January, 1942. The S.A.E. system was brought entirely into line with that of the Institute, except that the former still does not use the prefix letter specifying the type of steel-melting practice, and each body continued to use its own specifications for stainless steels.

Early in 1941 a shortage of nickel began to be felt, and in May the Institute published " Contributions to the Metallurgy of Steel—No. 1: Possible Substitutes for Nickel Steels." The report recommended the use of chromium, molybdenum, and vanadium instead of nickel in ferritic steels, and contained data showing the physical properties and hardenability U-curves of the nickel steels and their proposed substitutes. The carbon-manganese steels, containing 1·60–1·90% manganese, were not suggested at that time on account of the prevailing shortage of manganese. The recommendations for the use of chromium and vanadium instead of nickel soon proved premature, because within a few months these alloys had also become scarce. Molybdenum alone remained plentiful, and had the further advantage of being mined domestically. The experience of American manufacturers with straight molybdenum steels was still somewhat limited, although the Amola series, containing 0·20–0·30% molybdenum and about 0·70–0·90% manganese, had been in existence for several years. The Amola steels had proved successful for many carburised parts, including automotive transmission gears. However, in the thorough hardening grades the addition of about 1% chromium was preferred in many cases, in order to obtain greater depth of hardness and greater uniformity from one heat to another. For a long time the Amola steels were unofficially regarded as National Emergency steels, because they then represented the ultimate in conversation.

Shortage of Manganese

One of the most critical problems confronting the American steel industry during the early part of the war was the shortage of manganese. An annual production of 90,000,000 short tons of steel ingots requires about 1,500,000 tons of manganese ore containing 50% manganese. Under normal conditions, nine-tenths of this would have to be imported from Russia, the Gold Coast, India, Brazil, and Cuba. Although the Russian source of supply was cut off soon after the war began, imports from the remaining countries were such that 88% of the American supply of manganese was obtained from abroad in 1942. Regarding domestic sources, the Butte, Montana, and Las Vegas, Nevada, mines have now been developed to produce 170,000 and 130,000 tons per year respectively. The present annual production from other domestic sources totals about 30,000 tons.

An account of the manganese situation, entitled " Contributions to the Metallurgy of Steel—No. 3: Problems Involved in the Conservation of Manganese," was published by the Institute in October, 1941. The

uses of manganese in various types of steel were reviewed, and it appeared that in some cases manganese could easily be conserved, while in others no savings could be made without introducing serious problems in production or fabrication. The report concluded that about 10% of the manganese consumption could be saved without great difficulty, but that a reduction of more than 20% would cause a considerable decrease in output or quality. One of the largest savings advocated by the report was effected in 1942, when a plain carbon, heat-treated steel was substituted for the high-manganese high-sulphur steel used in the as-forged condition for the manufacture of artillery shells. This change was delayed until the necessary heat-treating equipment had been installed. The steel mills were also making experiments to conserve ferro-manganese. One method was to use spiegeleisen instead of ferro-manganese, since the former is made from domestic ores. As a further step towards conservation, a group of National Emergency plain carbon steels was adopted, differing from the standard steels only in that the manganese range was 0·10% lower, except in a few low-carbon steels, in which 0·50% maximum, with no lower limit, was specified. These steels are used mostly in the sheet, plate and structural grades, and have not been widely employed for high duty applications.

First NE Steels

The first National Emergency, or NE, steels were proposed in January, 1942, in a report to the Office of Production Management, predecessor of the War Production Board. The report was made by a group of metallurgists representing the Institute and the S.A.E., and was entitled " Contributions to the Metallurgy of Steel—No. 5 : Possible Alternates for Nickel, Chromium and Chromium-Nickel Constructional Alloy Steels." The steels proposed are known as the 8000 series, a group number which was not then in use in the classification adopted by the Institute and the S.A.E. The series included eight manganese-molybdenum steels in the 8000 to 8500 series, containing 1·00–1·30% to 1·30–1·60% manganese and 0·10–0·20% to 0·40–0·60% molybdenum. These steels should be compared with the existing manganese-molybdenum, or Amola, series. The steels also included eight nickel-chromium-molybdenum steels in the 8600 to 8900 series, all of which contained 0·40–0·60% nickel, 0·40–0·60% chromium, and about 0·75–1·00% manganese. The two steels of the 8600 series contained 0·15–0·25% molybdenum ; the four steels of the 8700 series contained 0·20–0·30% molybdenum ; and 8817 and 8949 contained 0·30–0·40% molybdenum.

The nickel-chromium-molybdenum steel compositions are based on the principle that the effect on hardenability of several different alloying elements of equal hardening power is greater than that of the same total amount of any one of them. This is because the effect of nearly every alloying element is proportional to its percentage by weight. Another aim in adopting multiple alloy steels was to reduce to a minimum the amounts of virgin ferro-alloys required, by taking advantage of all the residual elements contained in the scrap. Moreover, scrap from steels containing large amounts of one or two alloying elements caused high residuals when remelted. The high residuals particularly hindered the production of carbon steels, because in the manufacture of alloy steels the residuals could often be made to serve a useful purpose. Automobile manufacturers are being advised to redesign the bodies of their post-war cars to use the lower grades of deep-drawing steel that result from alloy contamination. This is particularly serious, because most companies plan to resume production with their latest pre-war models, in order to hasten the reconversion as much as possible. Finally, heats of the simple alloy steels had frequently to be diverted because the unspecified residuals exceeded the maximum amounts permissible—namely, 0·35% copper, 0·25% nickel 0·20% chromium, and 0·06% molybdenum. A check, by one large steel producer for the second quarter of 1942, showed that the average residual nickel contents in chromium-molybdenum grades were 0·22% in the open hearth and 0·20% in the electric furnace ; the residual chromium contents in nickel-molybdenum grades were 0·17% and 0·23% respectively ; and the residual molybdenum contents in nickel-chromium grades were 0·06% and 0·05% respectively. Trouble was also experienced from high copper and tin residuals, and many steel mills installed spectrographs to aid in their rapid analysis. The tin was derived chiefly from cans which, due to the shortage of scrap, were being returned to the mills so rapidly that the tin did not have time to corrode away. A number of detinning plants were in operation, but their capacity was insufficient to handle the full volume of cans in circulation. It should be noted that the rising residuals were not encountered to such a large extent in many of the lower quality steels, because these were increasingly being made on " flush " practice. In a flush heat about 60–70% hot metal (molten pig iron) and scale or iron ore are charged into the basic open-hearth furnace. The result is a high foamy slag, much of which is run off through a special slag notch. However, flush practice is not widely applied to alloy steels, owing to the difficulty of proper slag control. In such steels the high residuals were caused by several factors : the use of long dormant automotive iron and steel scrap ; the manufacture of the older highly alloyed steel during the early part of the war ; the comparatively low yield of useful product during rolling, forging, and machining operations ; the large amounts of steel required for test-pieces ; and inadequate scrap segregation at points of origin and collection.

The report recommending the NE 8000 series also contained results of hardenability tests on the new steels. The results of further hardenability and tensile tests were published in a series of data sheets put out by the Institute as supplements to the " Steel Products Manual, Section 10 : Alloy Steels." The hardenabilities were all measured by the Jominy end-quench test, which is now the standard method in the United States. It has been recognised that steels with the same hardenability characteristics may safely be substituted for each other, at least as far as tensile properties are concerned. Other properties, such as corrosion resistance, low-temperature impact strength, machinability, and abrasion resistance, are specific functions of the alloying elements. An excellent account of the effects of different elements of these properties was published in May, 1942, entitled " Contributions to the Metallurgy of Steel—No. 6 : Selection and Conservation of Alloying Elements Used in Steels." This paper was written by Mr. John Mitchell, and was mentioned in METALLURGIA, vol. 28, No. 165, page 138 (July, 1943). The paper serves as a guide to the selection of steels in those cases where there are other requirements besides the tensile properties.

The substitution of NE steels for the standard compositions took place rapidly, and was promoted by the armed forces, the steel manufacturers, and the steel consumers. Instrumental in the rapid adoption of the NE steels was the publication of results of tests on hardenability and physical properties. Case histories of successful substitutions helped further to gain recognition for the steels. By August, 1942, the production of NE steels had reached 180,000 short tons per month.

Revised List of NE Specifications

In September, 1942, a revised list of NE steel specifications was published. The usual rule was to add new and eliminate old grades rather than to change the limits of analysis of the existing steels, in order to prevent confusion as to whether the new or the old grade was intended. It was also decided to include in the NE steels all new and old alloy steels which contained the least possible amounts of nickel, chromium and molybdenum. Of the old alloy steels, the five high manganese steels from 1330 to 1350 were now included in the NE steels, but 1320 was not, chiefly because this grade has not met with much favour for carburising purposes. Also included were the silicon-manganese spring steels and the high-carbon-chromium ball-bearing steels. Several steels were eliminated in the manganese-molybdenum grades of the NE 8000 series—namely, 8124, 8233, 8245, 8447, and 8547, while 8024 was replaced by 8020 and 8022. The 8124, 8233, 8245 and 8447 grades had not met with great favour, while it was felt that 8547 did not represent good conservation practice because of the high molybdenum content.

Until the summer of 1942, it had appeared that sufficient molybdenum would always be available, so that changes to molybdenum grades were made wherever possible. The efforts to use molybdenum in place of nickel and chromium proved so successful that a shortage of molybdenum soon developed, particularly because molybdenum replaced tungsten in the manufacture of high-speed tool steels and armour-piercing shot. Exports to England and Russia further reduced the amount of molybdenum available for constructional steels. Reflecting the popularity of the multiple alloy steels, the number of grades in the nickel-chromium-molybdenum steels of the 8600 and 8700 series was increased. Five types of 8600 steel and seven types of 8700 steel were now made available. On the other hand, 8817 was eliminated, while 8949, recommended for large sections only, remained. An entirely new group of steels was proposed in the 9400, 9500 and 9600 series, with the aim of still greater savings in nickel, chromium and molybdenum. All of these steels contained 0·40–0·60% silicon, and hence were placed in the 9000 series, since the standard silicon range for the A.I.S.I.-S.A.E. alloy steels is 0·20–0·35%. The steels also contained appreciable amounts of manganese—in the 9400 steels the manganese ranged from about 1% in the low carbon grades to about 1·5% in the high carbon grades ; the 9500 steels, recommended for large sections only, contained 1·20–1·50% manganese ; the 9600 steels contained about 1·5% manganese. In addition, the ten steels of the 9400 series contained 0·20–0·40% nickel, 0·20–0·40% chromium, and 0·08–0·15% molybdenum. The four steels of the 9500 series, ranging from 9537 to 9550, contained 0·40–0·60% nickel, 0·40–0·60% chromium, and 0·15–0·25% molybdenum, so that they were identical with the 8600 to 8900 steels except for higher

manganese and silicon and lower molybdenum contents. The seven steels of the 9600 series comprised 9630 to 9650, and contained 0·40–0·60% chromium, but no nickel.

Soon after the 9400, 9500 and 9600 series compositions were published, directives were issued requiring tests to be made to determine their suitability for the various ordnance applications then using steels with higher alloy contents. A co-operative test programme between the Army and the steel manufacturers and consumers was begun, so that sample parts could be obtained with the least possible delay. The Iron and Steel Committee of the S.A.E. War Engineering Board was instrumental in co-ordinating the tests carried out by the truck manufacturers, and also assisted in advising the U.S. Army Ordnance engineers regarding substitutions in guns, tanks, and other material of Ordnance design.

Further Revision

The next revision of the NE steels was published in December, 1942. In all nickel-bearing NE steels the maximum nickel content was raised 0·10%, the lower limit remaining the same. This revision was made because the gradually increasing nickel residuals would otherwise have caused more heats to be diverted to the high nickel steels. NE 8022 and 8339 were withdrawn leaving only 8020 and 8442 in the manganese-molybdenum grades. The number of 8600 grades was increased from five to eleven, so that the series now extended from 8613 to 8650, because the entire 8700 series was cancelled, except for 8720. The reason for this change was the now serious shortage of molybdenum, but 8720 was retained as being the only NE steel that was satisfactory for some carburised parts. To conserve molybdenum further, 8949 was also withdrawn. Thus far the published data on the 9400, 9500 and 9600 steels had mostly been confined to hardenability tests. In March, 1943, the Institute published " Contributions to the Metallurgy of Steel—No. 10 : Mechanical Properties of the NE 9400, 9500 and 9600 Series," containing an account of mechanical property and hardenability tests on single heats of nine of the new steels. The heats were produced in a 300 lb. high-frequency induction furnace.

The revised list of National Emergency steels was published in August, 1943, with some significant alterations. NE 8020 and 8442 were eliminated, so that no manganese-molybdenum steels remained. Also, the composition of the 9400 series steels was considerably revised. The silicon content was reduced to the standard range of 0·20–0·35%, so that the original reason for placing these steels in the 9000 series no longer exists. To maintain the hardenability at approximately the same level, the nickel content was raised to 0·30–0·60%, and the chromium content to 0·30–0·50%. These changes in composition were made in consultation with the larger alloy steel producers and consumers, in whose opinion no further testing would be required in most cases to determine whether the new specifications would be satisfactory. The objects of the changes were to permit greater flexibility in handling alloy steel scrap, and to overcome some objections to the 9400 steels for carburising applications. The carburised cases were often found to contain an intergranular precipitate, which was at first thought to be graphite caused by the high silicon content. A later investigation published by J. Welchner and R. W. Roush, " Supposed Graphite in Carburised NE and S.A.E. Steels,"[*] showed that the

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[*] *Metals Progress*. Vol. 43, No. 6, p. 889. (June, 1943).

precipitate was probably a silica-alumina mixture. The silicon range of the 9500 steels remained at 0·40–0·60%, since this series does not contain any carburising grades. The entire 9600 series was withdrawn, owing to the fact that these steels had not found widespread application.

Recent Developments

There have been several developments in the National Emergency steels during recent weeks. A reduction in the price of the 8600 and 8700 series is being considered, which would increase considerably their chances of survival after the war. The prices of the 8600 and 9400 grades are at present equal, and the change would lead to a decreased popularity of the 9400 steels. The mills are encountering much difficulty in making the 9400 series, because of the high residuals. The output of triple-alloy steels is now 46% of the total for all alloy steels, and it is estimated that a further 10% can be converted.

A number of interesting changes in the composition of the National Emergency steels available have been made. The 8700 series has been reinstated with the addition of some new grades. This series is now identical with the 8600 series, except that the molybdenum range is 0·05% higher. An increased number of grades in the 9400 steels has been available. In addition, three entirely new series have been proposed—namely, NE 9700, 9800 and 9900. The compositions of the new steels are shown in the attached table. The 9700 group is a triple-alloy series having hardenabilities similar to the 4000 series. The hardening characteristics of the 9800 series are about half-way between those of the 8700 and 4300 steels, in the thorough hardening grades. The 9900 series has the same chemical analysis as 8700 series except for greater nickel and less manganese content, so that the hardenabilities are approximately equal. Another group of new carburising steels has not been included in the NE steels because of their high alloy content. These are the five steels ranging from 9310 to 9320, all containing 0·45–0·65% manganese, 0·20–0·35% silicon, 3·00–3·50% nickel, 1·00–1·40% chromium, and 0·08–0·15% molybdenum. The alloy content is similar to that of the 3300 steels, except for the higher molybdenum and lower chromium contents.

Present Status of NE Steels

One way in which the success of the NE steels may be judged is by the number of uses to which they have been put. At the present time about one-third of the alloy steel output of the United States consists of NE steels. Another quarter of the output consists of steels whose requirements cannot be met by any of the NE series. Of the remainder, no change to NE steels has been made in some cases because of conservatism or the lack of sufficient information or experience. In other cases binary alloy steels can be made with such good economy of alloying elements that no change is advisable.

Among the applications for which the tensile properties of NE steels have proved unsatisfactory may be mentioned carburised parts made from low-carbon, high-nickel and nickel-chromium steels, such as 2317, 2515 and 3316. Substitution has also not been feasible in the case of highly stressed bolts employed at hardnesses above 400 Brinell. Further, the NE steels are unsuitable for those sections where the maximum depth of hardening is required. Finally, they have not been recommended for certain purposes where specific alloying elements are needed in considerable quantities to produce special

properties, such as low temperature impact strength, resistance to hot exhaust gases, and high temperature creep strength. For the same reason, no NE stainless steels have been proposed. However, in many cases the allowable minimum quantities of nickel and chromium in stainless steels have been reduced by about 1%. Also the use of manganese instead of part or all of the nickel in stainless steels has been developed with some success.

The value of the NE steels may also be weighed by the quantities of alloying elements they have conserved. In 1943, 4,250,000 short tons of NE steels were produced, as compared with a total of 13,100,000 tons for all types of alloy steels. It is estimated that the NE steels saved 24,000 tons of virgin nickel in 1943, at the expense of 8000 tons of manganese and 3000 tons of molybdenum, but with no increase in the use of chromium. In addition, 10,000 tons of nickel, 6,000 tons of chromium, and 2,000 tons of molybdenum contained in the scrap were put to useful service in the NE steels, whereas the residuals would otherwise have led to such conditions as excessive hardening and difficult machining and heat-treatment. About half the tonnage of NE steels now being produced consists of 8600 and 9400 steels, the output of the latter being in the lead by a narrow margin.

The conservation resulting from the use of the NE steels has been so great that there is now no particularly serious shortage of any alloying elements, in spite of the fact that the production of alloy steel is greater than ever before. Nor is any future shortage of ferro-alloys anticipated. In the April, 1944, issue of the " Material Substitutions and Supply List," published by the War Production Board, the only alloys listed as being insufficient for war plus essential industrial needs were nickel and columbium. Low-carbon ferro-chromium was the only ferro-alloy classified as just sufficient for for these purposes. Supplies of all other alloys were considered more than sufficient for essential uses.

Full credit for the relatively plentiful supplies of ferro-alloys must also be given to the new or enlarged sources in the United States and other countries in the Western Hemisphere. The case of manganese has been mentioned above. Increased production of nickel has been secured chiefly through expansion of existing operations. Imports of chromium have continued at a high level, but in addition the low-grade ores of California and Montana and the beach sands of Oregon have been made to yield a considerable tonnage. The facilities for producing molybdenum have been enlarged and, in addition, 20% of the present output is derived as a by-product from some Western porphyry copper operations. Vanadium continues to be imported from Peru, and its supply is supplemented by production from Colorado. The stoppage of tungsten imports from China was alleviated by shipments from South America and, to some extent, by domestic production. Some of these new sources of ferro-alloys will continue in production after the war, but it is probable that many of them will be closed.

Future of the NE Steels

In looking into the future of the NE alloy steels, we need only consider the 8600, 8700 and 9400 series, since most of the remainder have been standard for many years.

The high percentages of alloying elements in iron and steel scrap will probably persist for a number of years

REVISED LIST OF NATIONAL EMERGENCY ALLOY STEEL
COMPOSITIONS

(ISSUED BY AMERICAN IRON AND STEEL INSTITUTE, MAY 26TH, 1944).

Grade.	C.	Mn.	Si.	Ni.	Cr.	Mo.
NE 1330	0·28–0·33	1·60–1·90	0·20–0·35	—	—	—
NE 1335	0·33–0·38	"	"	—	—	—
NE 1340	0·38–0·43	"	"	—	—	—
NE 1345	0·43–0·48	"	"	—	—	—
NE 1350	0·48–0·53	"	"	"	—	—
NE 52100A	0·95–1·10	0·25–0·45	0·20–0·35	0·35 max.	1·30–1·60	0·08 max.
NE 52100B	"				0·90–1·15	"
NE 52100C	"				0·40–0·60	"
NE 8612	0·10–0·15	0·70–0·90	0·20–0·35	0·40–0·70	0·40–0·60	0·15–0·25
NE 8615	0·13–0·18	"	"	"	"	"
NE 8617	0·15–0·20	"	"	"	"	"
NE 8620	0·18–0·23	"	"	"	"	"
NE 8622	0·20–0·25	"	"	"	"	"
NE 8625	0·23–0·28	"	"	"	"	"
NE 8627	0·25–0·30	"	"	"	"	"
NE 8630	0·28–0·33	"	"	"	"	"
NE 8632	0·30–0·35	"	"	"	"	"
NE 8635	0·33–0·38	0·75–1·00	"	"	"	"
NE 8637	0·35–0·40	"	"	"	"	"
NE 8640	0·38–0·43	"	"	"	"	"
NE 8642	0·40–0·45	"	"	"	"	"
NE 8645	0·43–0·48	"	"	"	"	"
NE 8647	0·45–0·50	"	"	"	"	"
NE 8650	0·48–0·53	"	"	"	"	"
NE 8712	0·10–0·15	0·70–0·90	0·20–0·35	0·40–0·70	0·40–0·60	0·20–0·30
NE 8715	0·13–0·18	"	"	"	"	"
NE 8717	0·15–0·20	"	"	"	"	"
NE 8720	0·18–0·23	"	"	"	"	"
NE 8722	0·20–0·25	"	"	"	"	"
NE 8725	0·23–0·28	"	"	"	"	"
NE 8727	0·25–0·30	"	"	"	"	"
NE 8730	0·28–0·33	"	"	"	"	"
NE 8732	0·30–0·35	"	"	"	"	"
NE 8735	0·33–0·38	0·75–1·00	"	"	"	"
NE 8737	0·35–0·40	"	"	"	"	"
NE 8740	0·38–0·43	"	"	"	"	"
NE 8742	0·40–0·45	"	"	"	"	"
NE 8745	0·43–0·48	"	"	"	"	"
NE 8747	0·45–0·50	"	"	"	"	"
NE 8750	0·48–0·53	"	"	"	"	"
NE 9255	0·50–0·60	0·70–0·95	1·80–2·20	—	—	—
NE 9260	0·55–0·65	0·70–1·00	"	—	—	—
NE 9261	"	"	"	—	0·10–0·25	—
NE 9262	"	"	"	—	0·25–0·40	—
NE 9415	0·13–0·18	0·80–1·10	0·20–0·35	0·30–0 —60	0·30–0·50	0·08–0·15
NE 9417	0·15–0·20	"	"	"	"	"
NE 9420	0·18–0·23	"	"	"	"	"
NE 9422	0·20–0·25	"	"	"	"	"
NE 9425	0·23–0·28	0·90–1·20	"	"	"	"
NE 9427	0·25–0·30	"	"	"	"	"
NE 9430	0·28–0·33	"	"	"	"	"
NE 9432	0·30–0·35	0·90–1·20	0·20–0·35	0·30–0·60	0·30–0·50	0·08–0·15
NE 9435	0·33–0·38	"	"	"	"	"
NE 9437	0·35–0·40	"	"	"	"	"
NE 9440	0·38–0·43	"	"	"	"	"
NE 9442	0·40–0·45	1·00–1·30	"	"	"	"
NE 9445	0·43–0·48	"	"	"	"	"
NE 9447	0·45–0·50	1·20–1·50	"	"	"	"
NE 9450	0·48–0·53	"	"	"	"	"
NE 9722	0·20–0·25	0·50–0·80	0·20–0·35	0·40–0·70	0·10–0·25	0·15–0·25
NE 9727	0·25–0·30	"	"	"	"	"
NE 9732	0·30–0·35	"	"	"	"	"
NE 9737	0·35–0·40	"	"	"	"	"
NE 9742	0·40–0·45	"	"	"	"	"
NE 9745	0·43–0·48	"	"	"	"	"
NE 9747	0·45–0·50	"	"	"	"	"
NE 9750	0·48–0·53	"	"	"	"	"
NE 9763	0·60–0·67	"	"	"	"	"
NE 9768	0·64–0·72	"	"	"	"	"
NE 9830	0·28–0·33	0·70–0·90	0·20–0·35	0·85–1·15	0·70–0·90	0·20–0·30
NE 9832	0·30–0·35	"	"	"	"	"
NE 9835	0·33–0·38	"	"	"	"	"
NE 9837	0·35–0·40	"	"	"	"	"
NE 9840	0·38–0·43	"	"	"	"	"
NE 9842	0·40–0·45	"	"	"	"	"
NE 9845	0·43–0·48	"	"	"	"	"
NE 9847	0·45–0·50	"	"	"	"	"
NE 9850	0·48–0·53	"	"	"	"	"
NE 9912	0·10–0·15	0·50–0·70	0·20–0·35	1·00–1·30	0·40–0·60	0·20–0·30
NE 9915	0·13–0·18	"	"	"	"	"
NE 9917	0·15–0·20	"	"	"	"	"
NE 9920	0·18–0·23	"	"	"	"	"
NE 9922	0·20–0·25	"	"	"	"	"
NE 9925	0·23–0·28	"	"	"	"	"

On all basic open-hearth steels, 0·040 max. P, 0·040 max. S.
On all-electric furnace steels, 0·025 max. P, 0·025 max. S.

after the end of the war. The steelmakers will therefore
be obliged to continue melting the triple-alloy steels,
unless the maxima for unspecified residuals are raised.

which is unlikely. Most steel consumers who are now
specifying the triple-alloy steels will be well satisfied to
continue their use, at least as far as engineering and
fabricating properties are concerned. In many, but not
all, cases the machinability of these steels is better than
that of the original materials. However, the cost of the
triple-alloy steels is the greatest of the low-alloy steels,
due to the number of additions that have to be made, and
to the expense of sorting the scrap. The price of the
triple alloy steels will have to be brought into line with
that of the other low-alloy steels before they can compete
successfully after the war.

One drawback of the triple-alloy steels is that their
heat-treatment is not so foolproof as that of the older,
more highly alloyed steels. Better control has had to be
developed by means of new equipment, better
instrumentation, or training of personnel. New quench-
ing oils yielding faster cooling rates have had to be
employed. Also the carbon range had often to be raised
about 0·05% when using the 9400 series, as is customary
with the Amola steels. Without these changes the triple
alloy steels would not have gained such widespread use.
But once the changes were made, the steels became
popular enough to anticipate a continued demand
during peace-time.

Due to the growth of testing for hardenability, the
advantages of purchasing alloy steel on the bases of
hardenability rather than chemical composition are
being seriously considered. If this plan is adopted, the
triple-alloy type of steel will probably predominate for
several years, until the residuals have been reduced
through dilution of the scrap with pig iron.

It is doubtful whether the NE plain carbon steels
will continue to be made after the war. The manganese
ranges of the standard plain carbon steels have been
developed over a long period, and it is therefore reason-
able to suppose they will return when industry reverts
to the conditions under which they were established.

Some of the more significant papers on the NE steels
have been mentioned above. It would be impracticable
to list here all the important references on the subject,
but those interested will find a complete and up-to-date
bibliography in *The Review of the American Society for
Metals*, vol. 17, No. 1, pp. 4–5, January, 1944.

Personal

Dr. Edwin Gregory, M.Sc., F.R.I.C., M.I.E.I., has
been appointed chief metallurgist to Edgar Allen and
Co., Ltd., in succession to the late Mr. S. J. Hewitt.
For some years Dr. Gregory was a member of the
Metallurgy Department of Sheffield University. In
1937 he was appointed chief metallurgist to the Park
Gate Iron and Steel Co., Ltd., and in 1943 became
assistant director in charge of the Metallic Materials
Section of the Aeronautical Inspection Directorate of
the Ministry of Aircraft Production. Dr. Gregory has
extensive metallurgical knowledge and experience, and
his new appointment will enable him to bring this fully
to bear upon production for the war effort.

Mr. J. D. Beddows, B.Sc., has been appointed metal-
lurgist and technical assistant to Dr. E. G. West, of the
Wrought Light Alloys Development Association. Mr.
Beddows, who graduated at Birmingham University in
1931, has held a number of important posts in industry.

Examination of Some Oil Coolers, Radiator Structures and Oil Tanks of Various Enemy Aircraft

(Except where otherwise stated, the examination of the components has been carried out by the staff of the Royal Aircraft Establishment, Farnborough.

These reports constitute summaries of data resulting from the metallurgical examination of parts from enemy aircraft carried out at the request of the Committee on Non-Ferrous Parts in Enemy Aircraft. The parts examined represent various oil coolers, radiator structures and oil tanks, and the main results are detailed.

THESE summaries of data resulting from the metallurgical examination of enemy aircraft form part of an extensive amount of work carried out on behalf of the Committee on Non-Ferrous Parts in Enemy Aircraft. The main object of the investigations was to obtain data on the types and quality of materials used, methods of manufacture, efficiency of treatment to which parts had been submitted, together with any other information which might prove of value.

DO.18/D3, JUMO 205C ENGINE—ALUMINIUM OIL COOLER

The general appearance of this oil cooler is shown in Fig. 1. The photograph was taken after partial sectioning to show more clearly the general construction. The cooling tubes had an exposed length of 16 in., an outside diameter of 0·470 in., and a wall thickness of 0·040 in. (1 mm.). They had been arranged in 26 banks of three tubes each. The units of three tubes were joined together by sinking the ends to a depth of about ¼ in. into header pockets (A in Fig. 2). The union of the tubes to the pockets had been effected by what appeared to be a hard solder having a dark grey to black surface appearance, but which on removal of the surface film had the bright white lustre of aluminium. This joining material is indicated by S in Fig. 2.

The banks of tubes were assembled to form one unit by welding together the adjacent pockets (see arrows W in Fig. 1). The appearance of these welds suggested that they had been made in the normal manner—i.e., by the use of ordinary aluminium wire filler rod, and were therefore different from those described above. These welds are normally shielded from view by the cover dishes, one at each end of the tube assembly, shown in section at C in Fig. 2. The cover dishes were joined to the manifold by joints S1 (Fig. 2). The filler material at these joints appeared to be identical with that at joints indicated by S in Fig. 2, mentioned above.

The neck unit (threaded) constituted a relief valve body, and was attached by means of the same dark-coloured filler material. A centrally placed baffle in this unit is indicated by B in Fig. 2. The inlet

(*zulauf*) and return (*rücklauf*) (see Fig. 1) to the cooler are situated on either side of the relief valve body.

Chemical Composition

Samples of materials of the various component parts were analysed chemically. The results obtained are given in Table I.

TABLE I.
CHEMICAL ANALYSES OF CONSTRUCTIONAL MATERIALS.

Component.	Tube.	Header Pockets.	Cover Dish.	Relief Valve Body.
	%	%	%	%
Silicon	0·10	0·31	0·21	1·02
Iron	0·25	0·20	0·17	0·31
Copper	—	—	—	0·20
Manganese	—	—	—	0·79
Magnesium	—	—	—	0·80
Aluminium	—	Remainder	—	—

The material of the tubes, header pockets and cover

Fig. 1.—General construction of oil cooler from Jumo 205C engines.
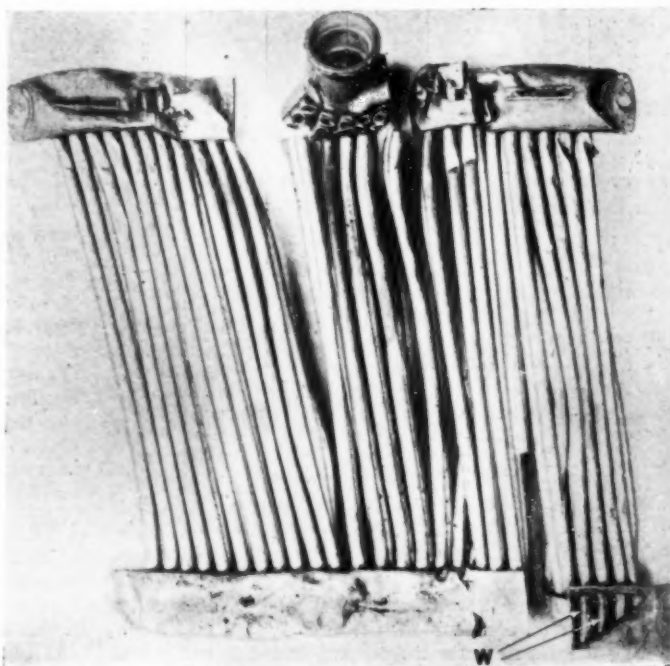
Fig. 2.—Details of oil cooler shown in Fig. 1.

Tensile and Hardness Tests

(a) *Tensile Test on Tube Sample.*—The following results were given by this test :—

Cross-sectional dimensions of tube, in.	0.471 o/d. $\times 0.041$
Maximum stress, tons/sq. in.	8.1
Elongation on 2 in., %	6
Elongation on 4 in., %	3

(b) *Hardness Tests* (HD/5).—The hardness tests were made on a joint made with the aluminium-silicon welding rod as well as on the materials of the components. The results obtained were as follows :—

	Hardness.
Weld metal	54, 55
Tube	36.2, 40.3, 41.0
Header pocket	21.6, 21.6
Cover dish	26.6, 26.6
Relief valve body	55, 55

Microscopical Observations

Polished sections from the various component parts and joints were examined microscopically. The structures of the parts were consistent with their chemical compositions. It was apparent from the grain flow around the walls of a header pocket that the part had been formed by a deep stamping or pressing operation. The relief valve body had been made by machining a bar or thick-walled tube.

Fig. 3 shows the structure of the aluminium-silicon weld metal in a typical joint. The dendritic formation of this material is characte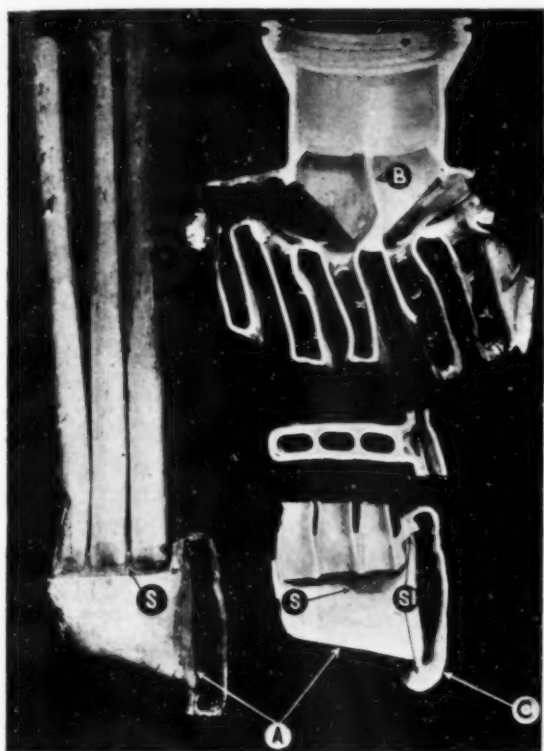ristic of cast aluminium silicon alloy containing about 10% of silicon. Effective union had been attained between the weld metal and the aluminium. This feature is also illustrated in the photomicrograph. The macrostructure of a section through one of the welds indicated by W in Fig. 1, is reproduced in Fig. 4. It suggests that the filler material has been

dishes was commercial aluminium. The relief valve body material was "Anticorodal." Similar material used in bar form in this country is covered by specification D.T.D. 423.

It was not practicable to carry out a complete analysis of the filler materials. Qualitative tests made on the filler material at joints such as are indicated by S and Sl (Fig. 2) showed that aluminium predominated and that there was a relatively high addition of silicon ; a small amount of iron was also detected.

Spectrographic Examination

Samples of the components shown in Table I and sample welded joints were examined spectrographically. The results obtained confirm those obtained by chemical analysis. No unusual element was detected. The filler material used for fixing the

Fig. 3.—Structure of weld metal in a typical joint. × 100.

Fig. 4.—Macrostructure of a section through one of the welds. ×6.

tubes in the header pockets and for attaching the cover dish to the manifold was an aluminium-rich alloy containing :—

Silicon	10 to 15%
Manganese	0.5 (about)
Magnesium	0.2 (about)
Copper	Trace

The weld metal used for connecting adjacent header pockets was relatively pure aluminium.

added to both sides of the bridge type weld. From examination of other welds, however, it is almost certain that the weld metal has been added from the right-hand side only, as shown in Fig. 4—i.e., the cover-dish side.

Welding Tests

In view of the excellent penetration and appearance of the joints in the cooler and of the probable composition of the filler material, it was decided to make

comparable joints in aluminium sheet, using a 12% silicon aluminium welding rod and ordinary aluminium rod. The trial joint was similar to those indicated by S1 in Fig. 2— i.e., where the cover dish joins to the header pockets.

Examination of the trial joints showed that the penetration of the silicon-bearing filler material was good, and similar to that in the cooler ; it was also much superior in this respect to that of plain aluminium wire. It is apparent that the temperature at which the silicon wire will flow is lower than the melting-point of the aluminium sheets.

In order to establish more precisely the flowing temperature of the silicon-aluminium filler material used in the assembly of the oil cooler a section with a transverse weld was suspended and heated in a muffle furnace. A weight of about 30 grms. was secured to the lower portion of the section in order to ensure separation at the joint when the melting temperature of the weld metal was reached. Separation occurred at 583° C. This temperature is very close to the melting-point of aluminium-silicon alloy of eutectic composition (11·6% silicon).

Fig. 5.—General appearance of a radiator from a Messerschmitt 109F.

Fig. 6.—A portion of a cooling tube from the radiator shown in Fig. 5.

temperature of about 58.°C., which is 60°–70° lower than the melting point of aluminium. It is considered that the execution of the design of the cooler was made possible by the successful use of this filler rod.
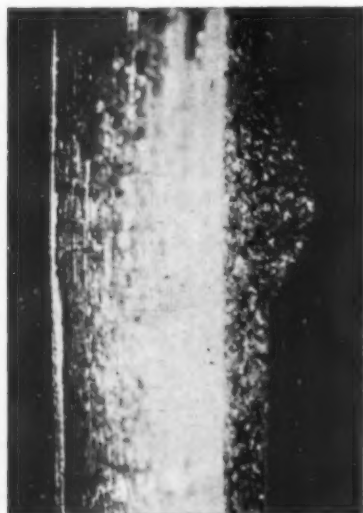

Fig. 7.—Section through one of the walls of a cooling tube. × 8.

Fig. 8.—An example of variation in depth of machining cut in making the cooling fins. × 30.

MESSERSCHMITT 109F, MERCÉDÈS-BENZ ENGINE—ALUMINIUM RADIATOR

The examination of this unit was necessarily non-destructive, as flying tests were being made on the complete aircraft. In general, the radiator was constructed of commercial aluminium, assembled by welding. The tubes were of oval section, approximately 8 cm. × 1 mm. internal dimensions, and were finned. The fins, which were about 0·5 mm. thick, had been produced by machining a solid drawn tube. The tubes were 1 mm. thick and the flat sides were kept apart by two inner longitudinal ribs, integral with the tube wall. No protective treatment appeared to have been applied. The general appearance of the radiator is shown in Fig. 5, and the outstanding features including overall dimensions are indicated.

The coolant normally employed is a 50% glycol-water mixture and not water. The proof pressure (machprufdr) of 0·75 (probably atmospheres) may refer to the cooling system as a whole rather than to the radiator unit, as the latter would be expected to withstand a considerably higher pressure.

The weight of the radiator was 58 lb., the frontal area 2 sq. ft., and the total surface area of the cooling tubes and fins was estimated to be 206 sq. ft. The area values

Comments

With the exception of the relief valve body, the component parts of the cooler are made from aluminium of ordinary purity ; the valve body material is Anti-corodal, an aluminium-rich alloy. The outstanding feature of interest from the point of view of material employed is the extensive use made of a silicon-aluminium alloy containing 10 to 12% of silicon, as a welding filler material. This material has a running
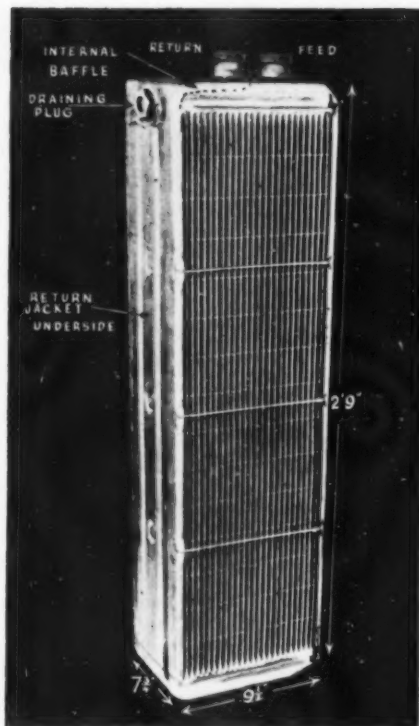
are understood to compare unfavourably with the corresponding ones for an earlier type copper radiator weighing 79 lb. on this type of aircraft. The frontal area of this earlier radiator was 1·61 sq. ft., and the total surface area 228 sq. ft.

Material and General Design

Some preliminary qualitative chemical tests showed that the material of the radiator gave the reactions of fairly pure aluminium. Detailed chemical analysis of material from the cooling tubes which became available during repairs showed the material to be commercial grade aluminium, containing 0·42% of iron as a primary impurity.

Diamond pyramid hardness tests on the tube material gave a value of 31. This value is of the order expected for fully annealed aluminium. The cooling block was composed of two banks of flattened tubes, one bank placed directly behind the other, in the air stream. These banks contained 24 tubes, each extending the full length. It will be seen from Fig. 6, which shows the appearance of a portion of a cooling tube, that the tubes were finned on the air side. The fins, 0·4 to 0·5 mm. thick, were spaced at a pitch of 2·5 mm., and had a mean depth of about 3 mm. The wall thickness of the tube was 1 mm., and the internal area of cross-section approximately 8 cm. × 1 mm. The tube was prevented from collapsing by two longitudinal ribs (R in Fig. 6) on the inside. A section through one of the walls of the tube in this region is shown in Fig. 7. Examination of a section from a tube, cut transversely with respect to the fins, showed that the fins were integral with the tube. A typical field from this section is shown in Fig. 8. The direction of the grain revealed by etching indicated that the fins had been formed by a machining operation involving the removal of the metal between adjacent fins.

In view of the thinness and low mechanical strength of the fins, it appeared probable that the machining had been effected with cutters, the cutting edge of which operated only on the bottom of the grooves between the fins. Similar samples examined recently had an appearance which suggested that the fins may have been produced by a swaging process.

Examination of the surfaces of the fins showed longitudinal grooves such as would be expected to result from this method of machining. The technique appears to be similar to that which has been employed by Langley Field (N.A.C.A.) for cutting close fins on light alloy muffs for air-cooled cylinders. Fig. 8 also shows the variation in depth of the machining cut, due, no doubt, to inaccurate setting of the cutters or control of the cut. The possibility of the tubes having been made from a sheet was examined. This is ruled out, however, by the absence of a longitudinal seam weld.

The adjacent tubes and banks were welded together at the top and bottom—i.e., at ends of tubes. The construction of the case which was built from sheet of 0·060 in. thickness also involved considerable welding. During repair of the damaged radiator, however, some difficulty in welding was experienced. The possible interference of some surface treatment was considered.
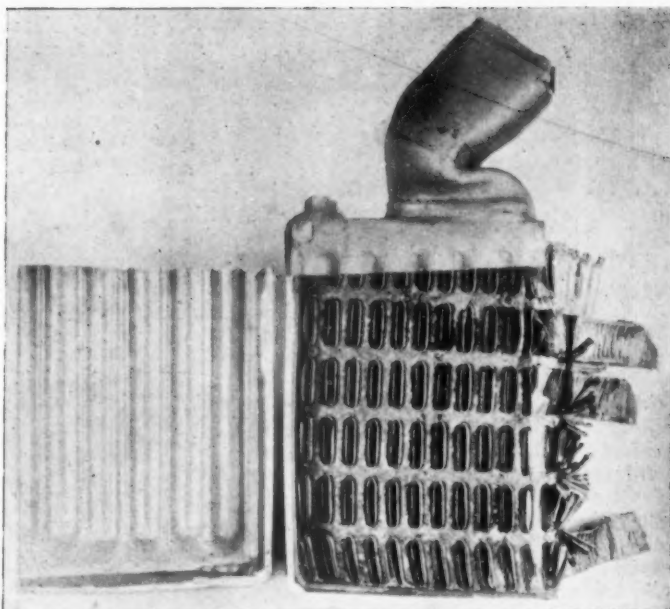
Fig. 9.—General appearance of part of the earlier type radiator from a Junkers 88. ⅓ actual s'ze.

There was, however, no evidence either of plating or anodic treatment, and the welding difficulty was eliminated by a prior cleaning treatment in a pickling bath. It was not possible to effect a complete repair of the radiator, however, owing to inaccessibility of some of the defective parts.

JUNKERS 88, JUMO 211 ENGINES—RADIATORS

Two different types of light alloy radiator from Junkers 88 aircraft have been examined. The general appearance of part of the earlier type, with some of the outer shell removed, is shown approximately third full size in Fig. 9. The radiator consisted of curved coolant tubes passing through flat fin-plates and end-plates into the headers. The coolant tubes were seamless, 26G thick, and were of rectangular section with rounded ends, the major and minor axes of the section being about 0·75 in. and 0·1 in. respectively. Deep die marks were found on the inner surfaces of the tubes.

The fin-plates were 0·008 in. thick and had been dimpled to maintain spaces between them. The leading and trailing edges of the fins had been folded in order to give stiffness. The tube holes in the fin-plates and end-plates had been punched, leaving lips which fitted round the tubes.

A section through the end-plate and two tubes is shown in Fig. 10. The ends of some of the tubes had been partly melted, probably during the welding of the tubes into the end plates.

The headers to which the end-plates had been welded consisted of light alloy sheet pressings lap-welded together. The weld metal appeared to be very similar to that used for setting the tubes in the end-plates, and had a dark grey to black surface with a bright metallic lustre underneath.

The outside of the headers, the surfaces of the fins and outside surfaces of the tubes had been finished

Fig. 10.—Section through end plate and two tubes of radiator shown in Fig. 9. × 4.

with a good quality oleo-resin varnish lightly pigmented with aluminium powder, and which, judging by its hardness, had probably been given a low-temperature bake. The varnish had good adhesion, and varied considerably in thickness. Besides affording protection against corrosion, the varnish appeared to serve as a jointing medium between the fins and tubes. When the varnish was removed by a solvent, the surfaces of the radiator parts were seen to be dark grey in c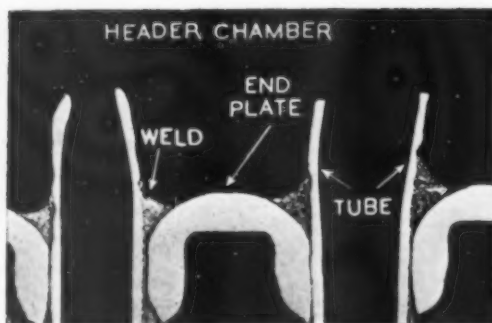olour. Spectrographic examination gave a strong indication of chromium at the surfaces, whereas the core materials were practically free from chromium. It was presumed that the radiator had been given a protective treatment similar to the M.B.V. process.

Spectrographic Analysis

Spectrographic analyses were made of the tubes, fins and sheets of the headers. The results showed that the tubes were made of commercial aluminium and the fins and sheets of aluminium alloy of the Anticorodal type. Aluminium alloy sheets of this type are covered by specification D.T.D. 346.

Hardness Tests

Diamond pyramid hardness tests made on sections of some of the components gave the following values :—

Header sheets	47 to 55
End plate	24 to 28
Weld material	67 to 71
Attached pipes	50 to 55

These values are usual for commercial aluminium and Anticorodal.

Microscopical Examination

Microscopical examination of sections of the various components showed that the structures of the parts were consistent with the types of material. The structure of the weld metal in all cases resembled that of a 10% silicon-aluminium alloy. The welds and weld metal were clean and sound in the sections examined. A thin layer of weld metal covered the entire surface of the end-plate on the header side. Microscopical examination together with the results of the above hardness tests suggested that the header sheets, attached pipes and fins were all of Anticorodal alloy, whereas the tubes and tube end-plates were made of commercial aluminium.

No corrosion of the materials used or of the weld metal had occurred.

Welding

Examination of the welds on the header and round the attached end-plates and pipes suggested that they had been made with oxy-acetylene, using a filler rod of aluminium containing about 10% of silicon. The workmanship was fairly good. The tubes had been attached to the end-plates by "torch brazing," using a 10% silicon-aluminium alloy as brazing material.

Second Radiator Examined

The second type of Junkers 88 light alloy radiator was examined for the Ministry of Aircraft Production by Birmetals, Ltd. A general view of one segment is shown in Fig. 11. The examination showed that sound but ingenious and unusual construction methods had been used. The main design consisted essentially of 24
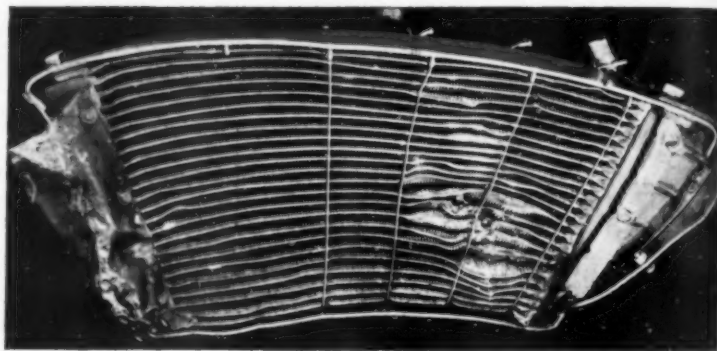
Fig. 11.—General appearance of a segment of a later type radiator from a Junkers 88.

aluminium tubes on which fins 0·125 in. apart and 0·0125 in. thick had been machined. The tubes had been flattened to a bore of $5\frac{1}{4}$ in. × $\frac{1}{16}$ in., and bent to form an arc equal to approximately one-fifth of a full circle. The adjacent ends of the tubes were welded together, and the group of tubes was welded at each end to small feeder tanks fabricated from pressed and welded aluminium alloy sheet. Except at the ends, the tubes were separated from each other by sheets of foil 0·0035 in. thick. At some stage in the flattening of the tubes a series of uniform and parallel waves had been formed in the fins, probably by pressure.

At first sight the method of construction would appear to be costly from the point of view of machine and man-hours, but further study suggests that with the necessary tooling equipment this type of construction would offer no serious difficulties in mass production. As an assembly it leaves the impression that it would be very much more resistant to the type of mechanical damage which can be expected from service conditions than are radiators of the usual construction made from thin gauge copper tubes and strip.

The assembly of tubes and tanks was encased in a covering strip of aluminium alloy material 6 in. wide × 0·160 in. thick. A view of the assembly with the covering removed is shown in Fig. 12. The covering strip consisted of two portions, one of which was bent over at right angles at the ends and the two sections were joined at these points by zinc-coated countersunk screws. The outer portion of the covering had inserted centrally at each end and projecting outwards, a small cylindrical zinc-coated sheet steel pressing, probably a location device.

The outer and inner surfaces of the sheet metal casing were prevented from distorting by means of six radially located steel spokes on each side. These were fitted into countersunk holes at the inner surface of the assembly and were tightened by screwed nipples on the outer surface. The dimensions, weight, etc., of the radiator unit were as follows :—

1. Dimensions—Overall length .... 23 in.
   Overall width .... 6 in.
   Depth .... 9 in.
2. Weight—As received .... 26 lb. 8 oz.
   With skin removed .... 20 lb. 4 oz.
3. Operating conditions—Operating temp. .. 115° C. maximum
   Operating pressure 10 lb./sq. in. gauge (approx.)
   Test pressure...... 28 lb./sq. in. gauge (approx.)

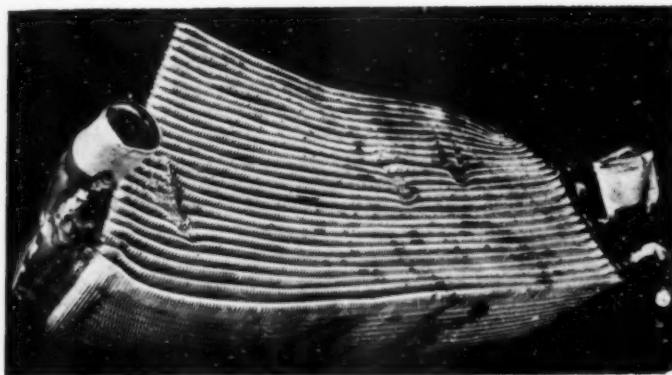The chemical compositions of the light alloy parts of this radiator are given in Table II.

Fig. 12.—The assembly of the radiator with cover removed.

TABLE II.
CHEMICAL COMPOSITIONS OF LIGHT ALLOY PARTS OF JU 88 RADIATOR.

Component.	Composition, %.				
	Cu.	Mn.	Mg.	Si.	Fe.
Sheet covering	4·16	0·46	0·93	0·48	0·36
Tubes	<0·01	Trace	Trace	0·245	0·18
Header tanks	0·02	1·23	Trace	0·26	0·37
Baffle sheets	<0·01.	0·31	0·96	0·98	0·37

The mechanical properties of the sheet metal cover were : 0·1% proof stress, 17 tons/sq. in. Maximum stress, 27 tons/sq. in. Elongation, 25–23%

From the metallurgical point of view there was nothing unusual in the various aluminium alloys which had been used. The tubes were pure aluminium of high quality in that their iron content was only 0·18%. The header tanks were made from typical D.T.D. 213 type of material. The baffle sheets between the tubes were of an alloy containing 1% magnesium and 1% silicon. The sheet-metal covering around the assembly was the Duralumin type alloy " Igedur." Micro examination of this latter material showed it to be of good ordinary quality with more striation than was desirable. Its iron content of 0·35% showed no indication of the forced use of large quantities of scrap or secondary metal. The covering had been anodised.

No detailed examination was made of the steel parts of the rubber hose connections, but the hose left the general impression that its fabric content was as high as possible and its rubber content as low as possible. It was noted that wherever there was contact between steel and light alloy the steel had been coated, probably electrolytically, with zinc.

FOCKE WULFE 200 (CONDOR) B.M.W. ENGINES—OIL COOLER

The appearance of this cooler, which weighed about 23 lb., is shown in Fig. 13. The frontal dimensions were 13 in. breadth × 6·6 in. maximum depth ; the other dimension, corresponding to the length of the cooling tubes, was 6·9 in. The tubes, which were of circular section 0·275 in. o/d × 0·0065 in. wall thickness, and expanded at the ends to a hexagonal form 0·318 in. across flats, had been arranged in six banks, corresponding to the divisions in the cooling space, visible in Fig. 13. It was apparent that the tubes had been assembled into blocks by dipping the ends in molten solder. The blocks had then been inserted in the casing. The casing consisted of an outer shell made from coated mild steel sheet, 0·030 in. thick, reinforced with straps of similar material, and an inner lining made from sheet brass, 0·011 in. thick, around the sides and bottom, but not along the top. The space between the outer casing and the brass lining was about ⅛ in. wide and was in series with inlet A and outlet C (Fig. 13). The space between the tubes was in series with inlet B and outlet C.

The banks of tubes were separated by steel strips 1 cm. wide and 1 mm. thick and also by thin brass sheets. The ends of the strips had been bent through a right-angle and small angle pieces of the same material had been copper welded to the ends to form I-shaped components that were riveted and soldered to the top and bottom of the casing The brass sheet was attached by riveting and soldering to the top and bottom of the casing alternately to form baffles.

Fig. 13.—General appearance of oil cooler from a Focke Wulfe 200.
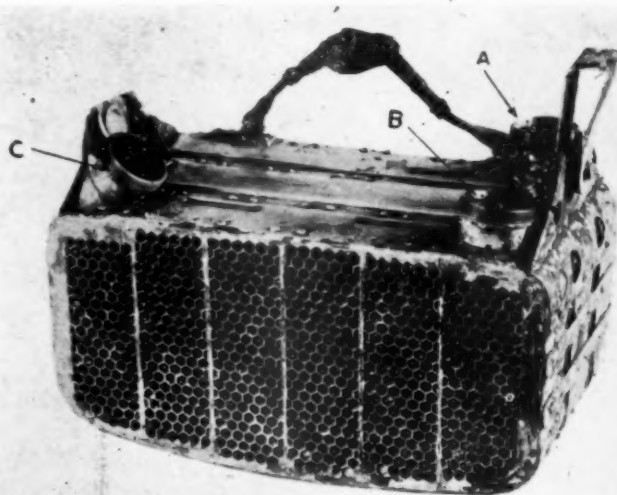
These baffles extended the full length of the cooling tubes and to two-thirds of the depth of the banks of tubes.

Chemical Tests

Chemical analyses of various parts resulted as follows : (a) Cooling tubes, 67·3% copper, 32·3% zinc ; (b) solder from cooling tube banks, 48·1% tin, 2·75% antimony, and remainder lead.

The coating on the mild steel casing contained 82% lead, 15·5% tin, and 2·5% antimony. It can, therefore, be regarded as a low-grade solder. The thickness of this coating was about 0·001 in. The rivets were of copper.

Comments

The tubes made from ordinary brass are assembled into individual banks by dipping in solder of the type normally used for automobile radiators, etc., and then inserted in the brass-lined casing. The use of a steel outer casing which has a thin protective coating of low-grade solder will not make for any appreciable saving in weight, but will result in economy in the use of brass, since the danger of corrosive attack by oil is considerably less than that of attack by engine coolants.

FOCKE WULFE 200 CONDOR ENGINE— OIL TANK

This tank was also made of light alloy, and had been covered with a self-sealing coating ; the whole was enclosed in a light alloy envelope the same shape as the tank proper. Its capacity was estimated at about 6 gals. The appearance after removal of the outer casing and self-sealing coat is shown in Fig. 14. A portion of a side panel has been removed to reveal the internal arrangement.
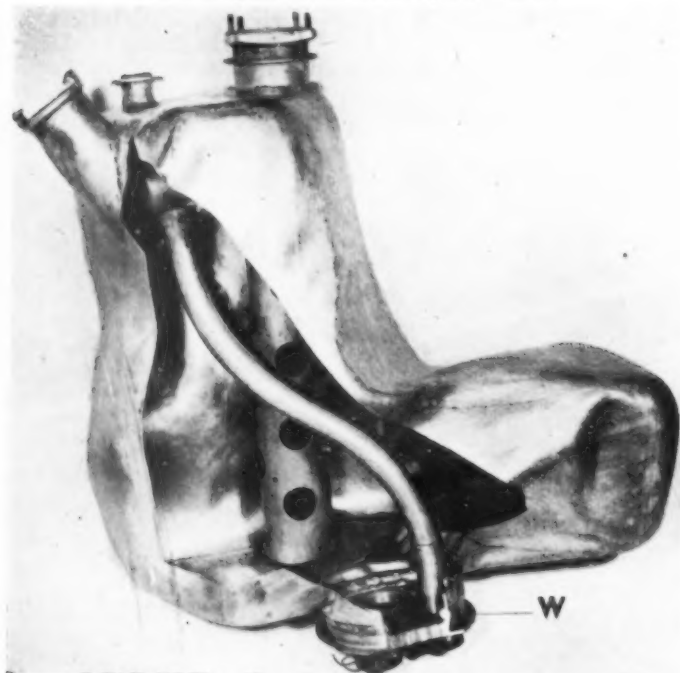
The tank shell was made from seven panels of soft light alloy 18G (0·048 in.) thick. The sheet had a bright finish on both surfaces, showing the absence of any protective finish. The outer surface, however, had been roughened with an abrasive such as coarse emery cloth. This may have been done in order to promote good adhesion of the self-sealing coat. The seven panels comprising the tank shell had been welded together by butt type seams which had a good appearance. The edges of the panels had been preformed to gradual bends, corner or edge welds being thus avoided.

The attachments incorporated in the shell consisted of one heavy gauge machined flanged unit in the base panel and three smaller units, including the filler throat, in the top panel. The weld joints between these attachments and the sheets were necessarily heavier than those joining the panels together, and there was a distinct difference in the surface appearance of the filler materials used. Microscopical examination showed that the filler material used for the heavy welds had a high silicon content, probably about 5 to 6%. The appearance of the section through the weld at W (Fig. 14) is reproduced in Fig. 15. The filler material in the panel welds was probably aluminium. It appeared probable that all the welding had been done by the oxy-acetylene torch method.

The outer envelope had been made in three parts, which hinged together, each part being separately assembled from panels of 22G (0·029 in.) and 20G (0·036 in.) sheets by gas welding. It had been painted on both surfaces.

Chemical Composition

Chemical analyses of samples from some of the component parts give the following results :—

	Si. %	Mn. %	Mg. %	Cu. %	Fe. %	Al.
(a) Tank shell....	0·18	Nil	—	Nil	0·39	remainder
(b) Flanged base unit	0·89	0·76	0·69	Nil	0·40	,,
(c) Internal tube .	1·16	0·75	0·84	0·20	0·42	,,
(d) Outer envelope	0·24	Trace	—	Nil	0·28	,,

Fig. 15.—Section through weld at W. × 5.

Fig. 14.—Oil Tank from Focke Wulf 200 with portion of side panel removed. × ⅛ actual size.
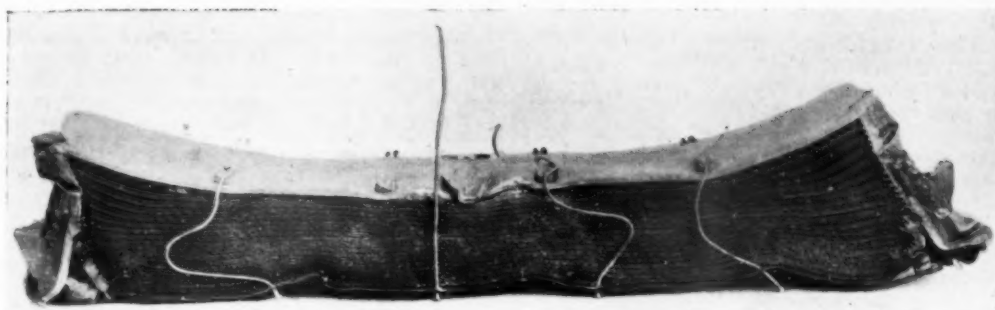
Fig. 16.—General appearance of complete radiator from a Messerschmitt 210.

It is apparent that the sheet material of the tank and outer envelope is commercial aluminium. The materials of the heavy gauge flanged base unit and of the internal tube are of the Anticorodal type, and are similar to that covered by specification D.T.D. 423. This material welds readily.

Hardness Tests

Vickers' hardness tests gave the following values :—

(a) Tank shell material	24·1	27·3	26·5
(b) Flanged base unit	43·4	43·0	—
(c) Internal tube	40·2	41·2	—

Hardness values in the range 24 to 27 are unusually low even for softened aluminium.

EXAMINATION OF RADIATOR UNIT FROM ME. 210

(Carried out in the Research Laboratory of Messrs. Rolls Royce, Ltd., for the Ministry of Aircraft Production.)

A general examination carried out on the radiator from an Me. 210 showed nothing particularly novel in the construction and materials, which were essentially brass, copper, low carbon steel and lead base solder. The brass used for the tubes appeared to be very soft, presumably for maximum ductility. There was no indication of corrosion.

Condition.—The complete radiator was very badly damaged, as shown in Fig. 16, in which one of the spoke ties has been straightened to show the original height. The centre was squashed to less than half the original height and both headers were burst open at the join to the end-plates by distortion. One of the coolant pipe connections was missing.

Mounting.—The top cover-plate was bolted to the underside of the upper wing surface by two bolts at the centre, the rubber washers between the two surfaces having acquired a permanent set. A strip of rubber ¾ in. thick, running the length of the radiator, was placed between the two surfaces. The ends of the radiator were suspended by means of a steel-faced rubber block and were attached to the wing bracing by two bolts at either end.

Construction.—Overall length, 43 in. Cooling length, 40 in. Original height, 12 in. ; Depth, 7 in. Weight empty, 135 lb.

The radiator consisted of brass tubes running from one header to the other. These tubes were ¾ in. wide by ³⁄₃₂ in. deep, made from 0·008 in. thick brass strip bent on a former to shape and the ends joined, as shown in Fig. 17, and the joint nipped together whilst on the former. The copper fins, 0·0035 in. thick, ran at right-

angles to the tubes from top to bottom cover-plate. These fins were alternatively straight and U-shaped between the tubes, as shown in Fig. 18. The headers were made of brass, the upper two-thirds being double sheet. The steel suspension brackets were copper riveted to the header. The cover-plates were connected by four spoke-type ties each side, and four brass strengthening ribs
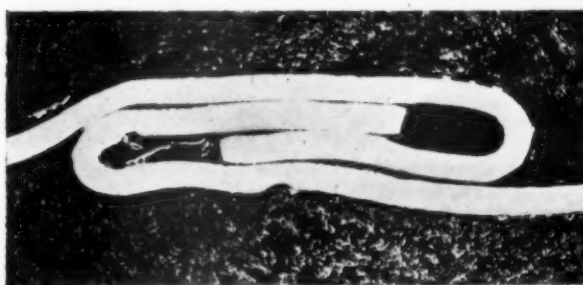

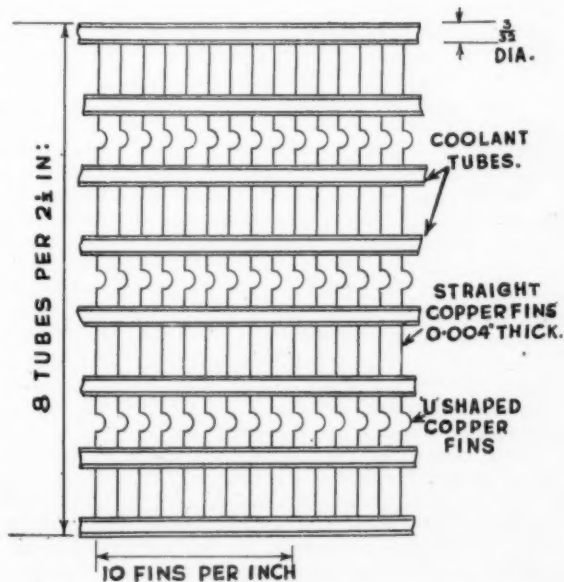Fig. 17.—Showing end joint of brass strip forming tubes.

Fig. 18.—Diagram showing construction of radiator from an Me 210.

were located at these points in the radiator. The radiator tubes, fins and end-plates were solder dipped. A soldered joint between a copper fin and brass tube is shown in Fig. 18. The interior surface of the tube was coated with solder. The headers were soldered to the end-plates, and the cover-plates soldered to the headers.

The results of chemical analysis and hardness tests on the various components of the radiator are given in Table III.

TABLE III.
CHEMICAL COMPOSITIONS AND HARDNESS VALUES OF ME. 210 RADIATOR PARTS.

Part.	Composition, %.										Coating.
	Cu.	Zn.	Sn.	Pb.	Sb.	Fe.	C.	Mn.	Ni.	Cr.	Hardness, etc.
Cooling fins	98·91	—	—	—	—	—	—	—	—	—	VPN/1 kg. = 35
Cooling tubes	71·32	29·36	Nil	—	—	Nil	—	—	—	—	VPN/1 kg. = 42
Strengthening rib ...	66·48	33·67	Nil	—	—	Trace	—	—	—	—	VPN/1 kg. = 56
Header	—	—	—	—	—	—	—	—	—	—	VPN/Brass 1 kg. = 75
Entry tube connection	—	—	—	—	—	—	—	—	—	—	Brass zinc coated
Cover plate	—	—	—	—	—	—	0·05	0·25	Nil	Nil	Tin-coated mild steel VPN/30 kg. = 130
Spoke tie	—	—	—	—	—	—	0·37	0·39	Nil	Nil	VPN/1 kg. = 126
Solder on tubes and pins.	—	—	29·5	70·0	Trace	—	—	—	—	—	—
Solder on pipe connection.	—	—	39·1	59·0	1·4	—	—	—	—	—	—
Solder on cover plate	—	—	40·1	59·0	0·69	—	—	—	—	—	—

Reviews of Current Literature

"Sheffield Burns"

DEDICATED to the people of Sheffield, past, present and future, this book by the late Dr. W. H. Hatfield is the result of an inspiration to devote the remainder of the author's life to help in restoring and rebuilding his native city after seeing it burn early one morning in December, 1940, and after finding, a few days later, the Research Laboratories, which had been his life for many years, blasted by enemy action. On reflection, he realised that his desire to contribute to the rebuilding of Sheffield was a very great task. His thoughts took him far afield, but his deductions all came back to the means whereby his native city could become happy and progressive.

Dr. Hatfield found it easy to conceive what he would like to do, but much more difficult to carry out the conception. It was necessary for him to reconcile himself to what he regarded as two apparently conflicting propositions : Man may be under a misapprehension when he believes that he is master of his own destiny. Nevertheless, he asserts, it is only by individual inspiration and enterprise that the new and better world will be brought into being.

In this book the author seeks to explain, as fully as he felt himself able to, matters which, expressed only in part, would probably be misunderstood. He writes on humanity, human beings and Divine discontent ; on reconstruction, in which he attempts to indicate future conditions of life ; and also on industry and science, subjects on which he naturally felt on firmer ground. The last chapter is an epilogue which sums up the author's deductions of a long period from careful observation and which should be carefully read to be appreciated fully.

Those who knew the author only as one of the outstanding metallurgists of his day will, on reading this book, have a deeper insight into his character and will appreciate the love he bore his native city and, in a wider sense, Britain and her people. He was troubled with the problems of life that the majority of us find so complex, but in some respects he had a clearer conception of them than have most of us. In the section on humanity, for instance, he says : " The spectres of humanity, irrespec-

tive of race or country, are war, ill-health, unemployment and famine. We of the Western world have been under the influence of Christianity for a thousand years ; the beauty and celestial nature of its teachings gain general appreciation and wide acceptance, but in practice our nations continue to slaughter each other in millions. The reason is simple, the spirit of mankind, capable of noble thought and tender solicitude, is for ever chained to the human body, and the human beings are part of animal life : we live by eating in the manner of horses, sheep and lions ; we are partly carnivorous, we feed in part on other animals, and it is only by the grace of God and the course of evolution that we buy mutton and sheep, not the human joints ; we are not as yet far from the jungle. There is collective good intention as regards other human beings, but inability to avoid disastrous clashes for material ends."

The chapter on human beings is much more intimate. Here the author writes of people, those with whom he was in constant contact over long periods, many with whom contacts were few, and also some rare and fortunate meetings through unforeseen circumstances. He regards it as a great thing for a young man to be fortunate in his early contacts, those who enjoy the game of life, that apply effort and experiences in an endeavour to achieve, rather than the actual achievements.

One is tempted to continue with the remaining chapters that are certainly not less interesting, but sufficient has been written to indicate that this book is well worth reading. It is regrettable that death prevented the author proceeding further with his ambition ; Britain, and in particular Sheffield, can ill afford to lose so brilliant a son, but there is much in this book which will help others to carry the torch and possibly bring to fruition some of the main views he presents. The final proofs were handed to the publisher just four days before the author died, and, owing to paper restrictions, the first edition was strictly limited and was exhausted by the complimentary copies presented by Mrs. Hatfield to the Doctor's personal friends. Fortunately, a reprint has been made possible, and copies are now available to the general public. It should be noted that Mrs. Hatfield has directed that all profits from the sale of this book are to be handed over

to St. Dunstan's, for men and women blinded on war service.

By Dr. W. H. Hatfield, F.R.S. Published by J. W. Northend, Ltd., West Street, Sheffield. Price 7s. 6d. net.

Development Reference Annuals
" Engineering Materials "
" Engineering Production "

THE above books comprise two volumes of a new series of annuals which have been published ; other volumes in the series are scheduled to be published as soon as possible. So much information is published on the various branches of engineering that progressive executives find it difficult to keep in touch with developments within their field. The object of these books is to provide references to enable the reader to locate the source of information regarding developments. Thus, in the volume on engineering materials a bibliography of literature published during past year or so and dealing with developments is given under each of the following subjects : Iron and steel ; non-ferrous metals ; precious metals ; natural and synthetic rubbers ; ceramics ; glass ; refractories ; plastics ; lubricating oils and greases ; solid fuels ; gaseous fuels ; and plywood and adhesives.

Edited by H. H. Jackson and published by Paul Elek (Publishers), Ltd., Africa House, Kingsway, London, W.C. 2. Price 8s. 6d. each volume, postage 6d. (abroad 1s.) extra.

Metals in the Service of Man

To deal with such a specialised subject as metallurgy for the man in the street is not easy, and it is probably more difficult for the specialist because the form of expression in conveying facts and opinions to another specialist on metals is very different from that necessary for the layman. In this case the authors are metallurgists ; they graduated at Birmingham University about twelve years ago, and since that time have had considerable experience and are well known in the world of metals.

The authors have rediscovered their youthful attraction and wonder for metals (if they were ever lost), and have applied their knowledge in such an admirable way that few who read this book can fail to be enthused by it. Metals are essential to civilisation as we know it, yet relatively few people know much about them. Even the engineer who depends largely upon metals has, in the main, only a hazy idea of the complexities of the numerous metals and alloys developed and applied to the service of mankind. It is not surprising, therefore, that those whose acquaintance with metals is more remote will be less familiar with many interesting aspects of what can be one of the most fascinating subjects. That the word fascinating is not misapplied will be appreciated by all readers of this book, however much or little they may be familiar with metals, because in preparing the script the authors appear to have been inspired. Indeed, it seems to the reviewer that the authors really enjoyed the preparation of this book, that their inspiration converted a difficult task into a pleasure.

This is a Pelican book, and is a credit to both authors and publishers. In addition to the interesting and informative text matter the book contains some excellent illustrations ; the line drawings especially are very instructive, and indicate that the artist responsible for them has caught the spirit of the authors.

We have no hesitation in recommending this book to the many who handle metals in their daily work, even metallurgists will find its perusal a welcome change from textbooks. Many copies should be made available to students in technical schools, particularly junior technical schools, where the spirit of the authors is likely to be absorbed sufficiently to cause many to make the study of metals their career.

By Arthur Street and William Alexander, with illustrations by Francis Coudrill. Published by Penguin Books, Harmondsworth, Middlesex. Price 9d. net.

White Metalling

THIS book deals with the mixing, melting, founding and machining of white metals for bearings, gland packings, etc. It presents information prepared to meet the needs of all who may be called upon to undertake various operations involving the use of white metal alloys, without having to make a search through the literature in which only brief reference is usually made. This information will be especially helpful in assisting the development of a satisfactory technique for relining white metal bearings, but the whole subject is admirably discussed and information is given that will be invaluable to those responsible for, or working in, repair shops where remetalling of bearings is occasionally necessary. The book is well illustrated, and many useful diagrams are included.

By H. Warburton. Published by Emmott and Co., Ltd., 78, Palatine Road, Manchester, 20. Price 2s. net.

Industrial Lighting Memorandum

THE advantages of good lighting have long been recognised by the more far-sighted industrialists, but it has needed a war, with its black-out and long working hours, to convince the rank and file that lighting is not just a necessary evil, an overhead charge to be kept as low as possible, but a tool with a direct and profound influence on both quantity and quality production. As war-time experience drives home realisation of this fact, the demand for improved lighting has grown and its benefits have become more and more recognised. Under war conditions, however, it is necessary to forgo many good things in order to have a sufficiency of those which are even more important, and with ever-increasing restriction the question is rightly asked : Is the installation of improved lighting justified under the special conditions now prevailing ?

This question is discussed from various angles and is answered in a memorandum of 20 pages, recently published, which will be found to be interesting as well as informative. Attention is especially directed to some Appendices which show the influence of lighting on the conservation of labour, speed of production, and the maximum use of raw materials, factory space and machine tools—all factors which are still of vital importance to the war effort. This memorandum may be obtained from the E.L.M.A. Lighting Service Bureau, 2, Savoy Hill, London, W.C. 2.

The Metallographic Examination of Aluminium Alloys

By N. H. Mason, G. J. Metcalfe, B.Sc., and B. W. Mott, M.A.

The procedure adopted at Royal Aircraft Establishments for the microscopical examination of aluminium-rich alloys is described in a recent paper* by the authors. Among the features dealt with are type of microscope, method of illumination of specimens, and methods of mounting and polishing specimens of alloys of different types. Some microstructural characteristics of cast and wrought commercial alloys are described, with particular reference to defects. The main features are given here in a substantially abridged form.

THE examination of aluminium alloys differs from that of steels and other alloys in the respect that most information is derived from examination of specimens in the unetched condition. The high reflectivity of a correctly polished aluminium alloy specimen accentuates any glare that may be present because of the lack of critical illumination, and to get rid of this glare it is usually necessary to reduce the diameter of the beam of light where the beam strikes the back lens of the objective. The result is that the resolving power of the objective is reduced and a spurious image is obtained. It is essential, therefore, that when examining aluminium alloys glare should be reduced to a minimum, and it should be possible to use a 2 mm. oil-immersion objective with a back lens filled with light. For a 4 mm. or 16 mm. objective the back lens should be about one-half or two-thirds filled, and in every case the beam of light should be central.

The type of illuminating train that has been found to give the best results is due to Greaves and Wrighton.[1] It enables the field of view and the diameter of the incident beam on the back lens to be controlled independently, and although it is usually considered to be necessary for use with a camera, the absence of glare and the simplicity of its construction have resulted in its being adopted for use with bench microscopes.

Preparation of Specimens

Since examination of specimens in the " as-polished " condition yields most of the information required, the specimen must be free from scratches, marked surface flow, and excessive relief of particles of hard constituents. If the specimen is so polished that the particles are in high relief, their colours cannot be distinguished, and examination of such a specimen will not yield the maximum amount of useful information. Methods of preparation described elsewhere[2, 3, 4] have been modified to give consistent results.

When necessary, the specimens are mounted in Wood's metal or a plastic. Two suitable plastics are phenol formaldehyde and methyl methacrylate. The specimen is polished on successively finer grades of paper and finished with a well-worn fine paper. Before the war Hubert's French emery papers were used, but recently specimens have been satisfactorily polished with Durex emery papers. The papers are used either dried or soaked in paraffin oil. The papers are placed on a smooth hard flat surface, such as steel or glass, from which all gritty particles have been removed.

* *Jour. Inst. Metals*, May, 1944, pp. 197-213.

Polishing is carried out so that all the scratches formed on the specimen by any one paper run in the same direction. Each time the paper is changed the specimen is cleaned to remove abrasive from its edges, and is turned through 90° so that the scratches formed are at right angles to those left by the previous paper. After preparation on the last paper, the specimen is polished by hand on a stationary velveteen pad that has been sprinkled with metal polish and moistened with white spirit. Final polishing to remove any remaining scratches is carried out on a second velveteen pad impregnated with alumina and moistened with water. This last stage is usually carried out on an automatic electrically operated machine.

Some aluminium alloys contain extremely hard particles in an excessively soft matrix. In such specimens the hard particles are liable to polish in high relief, with the result that it is difficult to detect their colour and shape. Excessive relief can be got rid of by continuing the polishing on a pad of blanket felt, using magnesia and water. The fine scratches caused by this pad are removed during the final polishing on the automatic machine. Hard particles in overheated aluminium alloys are frequently removed during polishing, leaving cavities, unless special procedure is followed. To avoid loosening these particles, the preparation of specimens must be very carefully carried out.

Properties of Cast Alloys

Examination of alloys in the cast state is normally made either with a view to determining the quality of the material for use as a casting or for assessing the suitability of the material for hot working. The more common defects in castings which are likely to cause weakness are segregation of constituents, non-metallic inclusions, and porosity.

Segregation of constituents occurs to some extent in all types of castings, but is usually more marked in sand castings than in material cast in dies or chill moulds. It is not easy to assess the amount of segregation that would be liable to cause undue weakness in a casting, as some constituents have a more marked effect on the mechanical properties than others. Such constituents as $FeAl_3$, which usually separates out in acicular forms, may weaken the material considerably if allowed to segregate into plates or excessively large needles.

The hot-working properties of cast material are impaired by coarse segregation, marked porosity, or non-metallic inclusions. Particles which crystallise in

the form of long needles or large plates resist deformation and persist in the worked material, resulting in a reduction of tensile properties. This type of microstructure is undesirable, especially for pistons.

Cavities and non-metallic inclusions are revealed by radiographic examination, but in general this method cannot be used to identify the exact nature of the defect. Microscopical examination of sections taken through the affected areas can frequently distinguish between cavities due to shrinkage and those due to gas. In some cases, however, it is not possible to draw a definite conclusion. Microshrinkage, which is too fine to be revealed by routine radiographic examination, can be observed and examined on polished sections.

Defects Resulting from Faulty Manufacture

Extruded sections or tubes may show blistering on the surface after heat-treatment, due to laminations in the material, even though the normal temperature of solution treatment has not been exceeded. Forgings made from extruded bars of large diameters may show cracking on the surface after machining. Anodic treatment of such parts usually reveals an exceptionally large, uneven grain-size on the outside, although the grain-size in the centre of the forging is more normal and uniform. The cracks are intercrystalline and occur at the boundaries of the very large grains. Microscopical examination shows that the cracks only extend to the same depth as the layer of coarse crystals. It is considered that the cracks are due to the relief of internal stress in the layer of coarse grains during machining.

A defect that may occur in Duralumin and which is said to be due to incomplete mixing and stirring of the molten metal is the formation of the iron-bearing manganese constituent in an acicular form. The acicular crystals are found near to the surfaces of extrusions and result in a reduction of the mechanical properties.[12]

The tensile properties in most of the commercial aluminium alloys are developed by suitable heat-treatment, comprising a solution heat-treatment at some temperature just below the solidus of the alloy and subsequent quenching followed by ageing at a lower temperature. Failure to heat-treat a part correctly may result in failure to develop the desired tensile properties and may give low resistance to corrosion.

The most common form of faulty heat-treatment is overheating, which results from exceeding the safe temperature of solution heat-treatment. Blisters and cracks may be observed on components which have been severely overheated, the extent of cracking depending to a large degree on the size and shape of the part, but in many cases the quality of the material may be impaired without any obvious defects being apparent on superficial examination. The detection of overheating in worked light alloys is therefore most important and can best be accomplished by microscopical examination.

The effects of heat-treatment at temperatures in excess of the safe range depend on the temperature attained, the period of treatment, and the subsequent treatment. The effects of overheating on the microstructure are influenced by chemical composition and the presence of segregation. Excessive segregation may result in the production of evidence of overheating after treatment at temperatures only slightly above or even below the recognised safe maximum. It cannot therefore be assumed that material which shows superficial evidence of overheating—e.g., cracks or blisters—has actually been heated above the specified temperature until microscopical examination has established that the alloy is free from excessive segregation or subcutaneous fissures. Evidence of overheating is found in a tendency for copper-red constituents to spheroidise or to liquate into the grain boundaries.

Material that has been annealed or has received no heat-treatment after hot working usually contains a large proportion of precipitated particles. Most of the common etching reagents, such as solutions of hydrofluoric acid, and a 25% solution of nitric acid at 70° C., may be used for revealing precipitation. A solution which has been found to be satisfactory for wrought alloys is one containing 25 ml. hydrochloric acid, 8 ml. nitric acid, and 7·5 ml. hydrofluoric acid per litre of solution. Grain boundaries can usually be revealed by one of the foregoing reagents, but the best reagent for a particular alloy in a certain condition is usually determined by trial.

Failures

The chief causes of failure of aluminium alloy components are : (a) Overstressing ; (b) fatigue ; (c) corrosion ; (d) corrosion accompanied by stress ; and (e) use of faulty material.

Microscopical examination frequently indicates the cause of failure or provides evidence of a confirmatory nature. Components that have fractured as a result of overstressing in tension, bending, tearing, etc., show distortion of the grains at the fracture. Such fractures in sound material are chiefly transcrystalline and follow a somewhat irregular path. Fatigue fractures, on the other hand, although transcrystalline, are fairly straight. Bacon[13] has discussed very fully the causes of increased liability to fatigue failure and particularly emphasised the effects produced by changes of section.

Unless aluminium alloy parts have been anodically treated or coated with protective paint, they are liable to corrode fairly rapidly, particularly in saline atmospheres. The types of corrosion encountered may be divided into three classes : (a) Normal pitting corrosion ; (b) intracrystalline pitting corrosion; and (c) intercrystalline corrosion.

Where the grains and grain boundaries are apparently attacked at approximately equal rates, the type of corrosion is known as pitting corrosion. Intracrystalline corrosion pitting is very similar to pitting corrosion, but is much rarer. The grain boundaries appear to be more resistant to attack than the interiors of the grains, with the result that an unattacked grain-boundary network is left in a corroded region. This type of attack was found in a sample of zinc-bearing aluminium alloy sheet that had been solution heat-treated at 460° C., quenched in cold water, and aged at 135° C.

By far the most dangerous form of corrosion is intercrystalline attack, in which rapid preferential corrosion of the grain boundaries occurs. This type of attack is found in alloys of the Duralumin type that have been aged at elevated temperatures or that are quenched from the solution heat-treatment temperatures at too slow a rate.[14, 15] Materials that are susceptible to this type of attack usually fail rapidly when the corrosion is accompanied by static stress. Failures that occur under these conditions are almost completely intercrystalline, and no distortion of the grains occurs at the fracture.

Failures that have resulted from the use of faulty material are, in the authors' experience, very small in number. Such failures have occurred owing to extrusion and forging defects, unsatisfactory grain disposition resulting in brittleness, excessive porosity in die-castings, cracks formed in castings during cooling due to incorrect feeding, and incorrect heat-treatment. Incorrect heat-treatment has been found to be the most common cause of failure of Duralumin parts, such as rivets.

Duralumin rivets are normally supplied in the unheat-treated condition—i.e., as-headed. They are quite soft, and before driving should be heated at 490°–500° C. and cold-water quenched. In the absence of low-temperature storage, they should be driven within 2 hours of heat-treatment, as the material age-hardens at room temperature. Sometimes, however, microscopical examination has shown that rivets that have failed have been driven in the condition as-headed. In the condition as-headed the mechanical properties of the rivets are low, and the material is very susceptible to inter-crystalline corrosion.

It is well known that quenching Duralumin in hot or boiling water after solution heat-treatment induces susceptibility to intercrystalline corrosion.[14] Delayed quenching also results in this susceptibility.[15] Of recent years corrosion failure of Duralumin owing to such unsuitable heat-treatment is comparatively rare, but occasional examples are encountered. Such an example is given of a transverse section at the leading edge of a Duralumin propeller blade, in which considerable intercrystalline corrosion had occurred, necessitating the scrapping of an otherwise sound blade. The mechanical properties of the material were satisfactory and heat-treatment experiments proved that the corrosion susceptibility had resulted from either quenching in hot water, or from quenching from too low a temperature.

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The Control and Composition and Heat-Treatment in 0.25 C, 1.5 Mn Steel Castings*

ACCUMULATED data on the 0·25 carbon, 1·5 manganese type of steel are given in this paper. A careful study was made following the production of the first 50 heats, which aimed at the desired composition of such a steel. The heats were produced in basic electric furnaces with a silicon content of 0·2 to 0·32, and sulphur and phosphorus under 0·035%. Contamination by other elements, such as nickel and chromium from the scrap was negligible. The final deoxidation practice yielded a fine grain size (McQuaid-Ehn 7 to 8). All heats were given the simple normalising treatment by which they were heated in furnaces at approximately 75° C. per hour. A temperature range of 900° to 940° C. was used for soaking ; the load was maintained at this temperature for 4 hours. No appreciable grain coarsening was found at/or slightly above 940° C. After soaking, the load was withdrawn and allowed to cool on the bogie.

Yield-point, ultimate stress and elongation results from the 50 heats indicated certain limits, from which the author draws the following conclusions :—(1) Ultimate stress shows a fairly consistent increase with rising carbon and manganese content, the former being much more potent ; (2) yield-point is relatively stable in the lower ranges, but begins to increase sharply in the regions of 0·27% carbon with 1·55% manganese. In this region air-hardening tendencies begin to develop, and (3) elongation shows a steady decrease with rising carbon and manganese, the decline being more marked above 0·25% carbon. The compositional limits finally adopted are shown in the form of a parallelogram on a carbon-manganese chart. Heats with analysis falling within this area can normally be expected to give satisfactory test results after standard heat-treatment.

Those falling outside were segregated, and either scrapped or given special heat-treatment.

The improvement in physical properties imparted by water-quenching and tempering is sufficient to warrant the most serious attention. The danger of cracking and warping, says the author, appears to have been over-stressed in the past, particularly in respect of the lower alloy or straight medium carbon steels. Also, excellent results have been obtained from both carbon-manganese and straight carbon steels with a quench directly from the first homogeneising treatment. Tests carried out to assess the advantages of the two methods are shown in Table I. There is appreciable gain in ductility and impact with the treble treatment, but some loss in yield and ultimate stress.

TABLE I.
INFLUENCE OF HEAT-TREATMENT ON THE PROPERTIES OF 0·25 C., 1·25 Mn STEEL.

Heat No.	% C.	% Mn.	Heat Treat-ment.	Yield-point, Tons per Sq. In.	Ultimate Stress, Tons per Sq. In.	% Elonga-tion.	% Reduc-tion of Area.	Izod, Average Ft.-lb.
C. 12,499 ...	0·25	1·46	" A "	40·00	49·15	20	42·5	45·8
" ...	0·25	1·46	" B "	36·70	46·70	23	51·5	44·7
A. 4,940 ...	0·24	1·25	" A "	29·10	40·98	25	45·5	52·8
" ...	0·24	1·25	" B "	28·30	39·40	29	52·0	54·5
B. 5,320 ...	0·31	1·08	" A "	30·00	43·65	25	48·5	55·3
" ...	0·31	1·08	" B "	29·75	41·70	28	56·0	61·5

* Heat Treatment :—" A "—4 hours 900–920° C., W.Q., 3 hour 550° C. Air cool.
" B "—4 hours 900–920° C. Air cool, 1 hour, 850° C., W.Q. 3 hours 550° C. Air cool.

THE Ministry of Supply has given notice that the arrangement announced in the Press on July 21, 1942, for the purchase of wolfram concentrates by Non-ferrous Minerals Development, Ltd., at Plympton, South Devon, will be terminated on December 31, 1944, and that no concentrates will be accepted by Non-ferrous Minerals Development, Ltd., after November 30, 1944.

*Paper by T. W. Ruffle before the recent Annual Meeting of the Institute of British Foundrymen.

The Rare Earths*

By R. C. Vickery, Ph.D., M.Sc.

A survey is given of the present position of the chemistry of the rare earth elements. Their nature is summarised and a general account given of methods of separation, identification and determination. Existing problems are considered, and many references to original work are given.

INFORMATION on the first group of the following compounds may be taken as being more complete than that of the second, but it is to the second group that more thought and work is being devoted, and it is to be hoped that within a few years our knowledge of organic compounds of the rare earths will be as complete as our knowledge of the inorganic acid salts of that group.

(A) As Salts of Organic Acids

(i) *m-Nitrobenzoic Acid.*—This reagent has been employed for the precipitation of thorium in the absence of ceric salts. Cerous, lanthanum, praseodymium, and neodymium salts do not interfere. Where separation can be effected by this means, it has been found that precipitation is more complete and occlusion less evident if aniline is present.

(ii) *Stearic Acid.*—Separation of the yttrium earths has been successfully carried out by the addition of alcoholic potassium stearate to a cold-saturated solution of the rare earth nitrates. The originators of the method[39] claimed that for the separation of yttrium from monazite the method was decidedly good, and the author, having used the method on several occasions, has found everything in favour of the reagent. The separation from the cerium metals which precipitate first is rendered complete in relatively few operations, and the cheapness and efficiency of the process commend the matter to further study.

(iii) *Sebacic Acid.*—For the removal of thorium, this reagent may successfully be employed in boiling solutions. Earths other than thoria are not precipitated even with prolonged boiling, whilst yttrium may be separated quantitatively from the rare elements by means of the ammonium salt.

Numerous other organic acids have been employed—succinic, valeric, cacodylic, phthalic, salicylic, are all known in the literature, as well as modifications of the crystallisation technique with oxalates, citrates, acetates, chloroacetates, butyrates, formates, etc.; but, as has been indicated above, it is the more complex organic bases which are now attracting attention :—

(B) As Complexes with Organic Bases

(i) *Aniline.*—According to Mellor,[31b] this has been used more than any other individual organic base. A neutral 50% alcoholic solution of the rare earth chlorides is treated with a 2% alcoholic solution of aniline ; or after partial precipitation by NH_4OH, aniline hydrochloride is added and the mixture digested at 60° C. Thorium being a weak base is precipitated entirely by this method, providing all the Ce is in the tervalent condition and the solution is exactly neutral before the drop-wise addition of the aniline.

(ii) "*Oxine.*"—Manelli,[40] after a comprehensive investigation of the precipitates obtained with 8-hydroxyquinoline, concluded that by proper control of the pH, Ce and Th could be easily separated by use of this reagent. The author has employed Manelli's methods and has found that in the absence of interfering elements, such as Al, Mg, etc., individual rare earth elements may be quantitatively separated as complexes of the type [structure] which are of definite composition, so that the method is applicable, as Manelli suggested, for the determination of certain of the rare earth elements. Further work has been carried out on this subject by Pirtea, Berg and Becker,[41] and providing the pH of the solution be carefully controlled, and operations be carried out after the rare earths have been separated as oxalates, it would appear that some attention might be paid to this process.

(iii) *Tannic Acid.*—The use of this reagent, recently revived by Schoeller and Powell,[38] in application to the rare earths, was investigated in 1935 by the former author and Waterhouse,[42] who estimated the rare earths gravimetrically in ammoniacal tartrate solution. In this case, as in others, precipitation is not confined to the rare earth group only, and several conditions of solution, pH, etc., must be complied with to procure reasonable results.

Schemjakin and his co-workers[36] have examined the reactions of the rare earths with pyrogallol and alkaloids. Fogg and Hess[43] have employed urea for the fractional separation of yttrium from its earths, and Das-Gupta[44] showed that the reactions of gallic acid with, *inter alia*, the rare earths were of interest. Other organic bases such as alizarin-3-sulphonate, 1 : 2 : 5 : 8 tetrahydroxyanthraquinone, ammonium aurintricarboxylate, ethylenediamine, o-toluidine piperidine, phenylhydrazine, benzidine, etc., have been variously suggested as reagents for the rare earths, but are not used for general separations ; though in special cases, and with small amounts of material, good results might be obtained.

3. Methods of Oxidation

These processes are mainly directed to the separation of Ce from the other rare earths, being based upon the fact that cerium alone forms a strongly electropositive trihydroxide $Ce(OH)_3$ and a feebly electropositive tetrahydroxide $Ce(OH)_4$.

39 Stoddart and Hill. *J. Am. Chem. Soc.*, **33**, 1076, 1911.
40 *Atti. X° congr. intern chim.*, **2**, 718, 1938.
41 Pirtea. *Z. Anal. Chem.*, **107**, 191, 1936 ; *Bull. chim. soc. Române*, **38**, 83 1938 ; Berg and Becker. *Z. Anal. Chem.*, **119**, 1, 1940.
42 *Analyst*, **60**, 284, 1935.
43 *J. Am. Chem. Soc.*, **58**, 1751, 1936.
44 *J. Indian Chem. Soc.*, **6**, 763, 855, 1929.

(i) *Thermal Decomposition of the Nitrates.*—This process has already been reviewed (v.s.), but a few more remarks may not be out of place. Simple ignition of the nitrates may be employed as such, or modified by the addition of alkali nitrates to the rare earth nitrate mixture. Decomposition is prolonged at 300°–350° C., whereby only Ce is converted to the oxide which is left when other oxides are leached out.

(ii) *Bromine.*—Originally, chlorine was employed for conversion of the rare earth hydroxides to soluble salts, leaving the cerium salts insoluble, but the substitution of bromine for this purpose was attended by marked advantages, although as recently as 1933 chlorine was still being employed for a similar process.[34]

(iii) *Per-salts.*—In neutral solution, oxidation may be carried out by the permanganate, persulphate, or peroxide of Na, and depends upon the conversion of the tervalent Ce compounds to the oxide CeO_2. With the permanganate, however, separation is preferably carried out in alkaline solution, and in any case it is necessary to have present a neutralising agent to remove the acids formed from the electronegative portions of the original salts.

In acid solutions—i.e., HNO_3 solutions of the nitrates— lead peroxide is employed in boiling solution. Several substitutes have been suggested for PbO_2, amongst them being red lead and bismuth tetroxide, and it appears that better results are obtainable by use of the Bi compound.

Hydrogen peroxide in ammoniacal solution will precipitate Th from a solution of the sulphates as $Th_4O_7.SO_3$, whilst the rare earths remain in solution. It is an essential feature of the separation that the H_2O_2 employed be free of such stabilisers as phosphoric acid, etc.

(iv) *Bromates.*—James has employed this method in his tables of separation (*vide* Table III). The solution in this case must also be kept neutral—e.g., with marble chips. The method is quite efficient and applicable, and gives consistently effective separations of Ce free of the other rare earth elements.

4. Physical Methods

(i) *Distillation or Sublimation.*—The application of this process to the halogen salts or the acetylacetonates, has not as yet proved to be of sufficient applicability to warrant general usage. The earlier workers, however, conducted several investigations on the subject, but their work was chiefly concerned with the separation of Sc and Th from the rare earth group elements.

(ii) *Electrolysis.*—A large amount of work has been, and is being, carried out on this promising project. Straight electrolysis of rare earth salt solutions has not yielded results of a promising nature. Electrolytic oxidation of the elements has been attempted, and use has been made of this process for the separation of cerium from monazite,[45] but even so, and in spite of the work of Yntema and Beck,[46] and of Hopkins and Audrieth,[47] on non-aqueous electrolytes, straight electrolysis remains a relatively unusable process. With the advent of the polarograph and dropping mercury electrodes, however, the position has become to a certain extent clarified, and the past decade has seen accomplished some notable work in this sphere. The conversion of the elements to amalgams not only effects a quantita-

tive separation when controlled potentiometrically, but from the resulting amalgam the pure metals may generally be obtained by heating in vacuo at 1,000° C. to volatilise the mercury and leave behind a residue of the element. Alimarin and Frid[48] have recorded failure when attempting to electrolytically separate the rare earths in acid solution, but in view of the success which has attended the efforts of other workers, it would appear that some factor was overlooked which, if noted, would have modified the negative result obtained. Results so far available are concerned mainly with the separation of Eu, Yb, Sm and Gd ; thus for the separation of Eu from Gd and Tb, Marsh[49] employed a cathode of of amalgamated lead, but other workers did not consider this necessary, and employed a pool of mercury or a dropping mercury column as the cathode.[50]

(iii) *Amalgamation.*—The employment of an electric current is not essential for the formation of amalgams ; they may be formed by displacement, as has been shown by West and Hopkins, who employed Na amalgam,[51] Holleck and Noddack[52] with Sr amalgam, and McCoy[53] who used K amalgam. Marsh also studied the use of Na amalgam, and subsequently employed the method for the separation of Yb from Lu and Tm.[54] The future of this method is still at present obscure, but it must be remembered that it is applicable only to such of the rare earth elements as form amalgams, although the differences of the elements in this respect might in itself form the basis of a method of separation.

(iv) *Adsorption.*—In 1893, Hoffmann and Kruss[55] suggested that separation of the rare earth elements might be accomplished by shaking the solution with " phosphate-free charcoal," the weaker bases being adsorbed first. As the amount of material removed from solution, however, was rather small (from 2 gm. of a mixture, 0·5 gm. was adsorbed by 8 gm. of charcoal), the method was not regarded as particularly applicable. In 1939, however, Botti published the results of his studies of the adsorption of the rare earth salts by activated carbon,[56] and found that the amounts of salts taken up were dependent upon the variety of the carbon and also upon the individuality of the element. His findings that Gd and Sm were more strongly adsorbed than Ce and Pr, are in agreement with those of the earlier workers. He concludes that the use of carbon for the separation of mixtures of small amount of the rare earths is practicable for those elements following Nd. In spite of this lack of general utility of the method, it is possible that the increasing amount of work on the applications of chromatography might lead to some definite results in this direction.

(v) *Partitional Solution.*—The use of the phenomenon of partition of the rare earth elements between two immiscible solvents appears to be of only recent introduction. Fischer, Dietz and Jubermann[57] stated that it was possible to find pairs of liquids between which the rare earth compounds will distribute themselves, and for which the partition coefficient is sufficiently large to enable reasonable separations to be made.

45 Atanasiu and Barbor. *Bull. sect. sci. acad. roumaine*, **20**, 27, 1938.
46 *Z. Angew. Chem.*, **52**, 536, 1939 ; *J. Am. Chem. Soc.*, **52**, 2782, 4264, 1930.
47 *Tr. Electrochem. Soc.*, **66**, 139, 1934.

48 *Zavodskaya. Lab.*, **8**, 496, 1939 ; *Chem. Zentr.*, II, 2789, 1940.
49 *J. Chem. Soc.*, 1972, 1934.
50 Pearce, Nesar and Hopkins. *Tr. Electrochem. Soc.*, **69**, 557, 1936 ; Brukl. *Z. Angew. Chem.*, **50**, 25, 1937 ; Jukkola. *J. Am. Chem. Soc.*, **56**, 303, 1934 ; McCoy. *ibid.*, **63**, 1622, 1941.
51 *J. Am. Chem. Soc.*, **57**, 2185, 1935.
52 *Z. Angew. Chem.*, **50**, 819, 1937.
53 *J. Am. Chem. Soc.*, **63**, 3432, 1941.
54 *J. Chem. Soc.*, 398, 1942 ; *ibid.*, 8, 1943.
55 *Z. Anorg. Chem.*, **3**, 89, 1893.
56 *Atti. X° congr. intern. chim.*, **3**, 406, 1939.
57 *Naturwiss.*, **25**, 318, 1937.

They concentrated generally upon the halides, but preliminary results have been submitted by other workers[58] who have fractionated La and Nd thiocyanates between water and butyl alcohol. The methods might repay further investigation, and if successful results are consistently obtained, would certainly facilitate a rapid separation of the rare earth elements.

Individual Characteristics

Cerium.—Owing to the relative abundance of this element as compared with the other rare earths, it is perhaps logical that more should be known of this element and its chemistry than of its associates. It might be considered advantageous also that one element predominates which incorporates in itself reactions and properties which are, generally speaking, equivalent to those of its congeners. Very many compounds of cerium have been prepared and investigated to varying extents, the amount of information available on any particular compound being probably directly proportional to its value in separation processes.

The comparative ease with which cerium may be separated from its allied elements is due to its property of forming tetravalent ceric salts—in particular the dioxide CeO_2—which are much less strongly basic than the tervalent compounds. Ceric salts are much more readily hydrolysed in solution than the corresponding cerous salts, and in dilute solutions show a great tendency to undergo reduction. The dioxide is obtained by the ignition of ceric salts, such as the oxalate, acetate, nitrate, etc., or by the ignition of the metal in oxygen ; it is attacked by HNO_3 or HCl only in the presence of a reducing agent. In the crystalline form, the dioxide exhibits great resistance to attack both by acids and alkalies. A further oxide Ce_4O_7 is known as a dark blue compound with strongly reducing properties. The hydroxide $Ce(OH)_4$ may be prepared from tetravalent cerium salt solutions in the usual ways, and may also be obtained by dialysis of a solution of a ceric compound.[5] The only halogen salt known in the free state is the fluoride $CeF_4.H_2O$, obtained from the interaction of HF and the hydroxide. Ceric sulphate $Ce(SO_4)_2$ is now becoming widely known and employed in sulphuric acid solution as an oxidising agent,[59] such solutions are however, always evolving oxygen and consequently are always contaminated by cerous compounds. Of the nitrate $Ce(NO_3)_4$ little, so far, is known, but the basic salt $Ce(NO_3)_3OH.3H_2O$ crystallises on evaporation of a nitric acid solution of the hydroxide. Hydrolysis of this salt in solution is very marked. The double ceric nitrates are very important in so far as separations are concerned ; they are deep red, hygroscopic compounds of the type $R_2Ce(NO_3)_6$ and the alkali double salts are more stable than those in which R represents metallic elements.

The cerous compounds are to a certain extent similar to those of the other rare earth elements. Ce_2O_3 has been prepared by reduction of the dioxide with calcium as it cannot be prepared by ignition of cerous salts of volatile acids. The hydroxide, however, may be prepared in the usual way by the addition of alkali hydroxides to solutions of cerous salts, but the compound is very sensitive to oxygen, being therefore relatively unstable. $Ce(NO_3)_3.6H_2O$ forms soluble colourless crystals, but the double nitrates assume more importance from the separational point of view. Carbonates and double carbonates may be prepared as stated above, by addition of dilute, or concentrated, solutions of alkali carbonates respectively.

The sulphides of both valencies are unobtainable by the passage of H_2S through solutions of ceric or cerous salts, but may be prepared by prolonged heating of the respective sulphates in H_2S at red heat.

Cerium metal, as obtained by electrolysis of the fused chloride is a white powder, but when worked up is steely-grey in colour, with a brilliant lustre, which tarnishes in moist air and slowly decomposes water with evolution of hydrogen. Its melting-point, according to Hanaman,[60] is about 720° C., but the metal ignites in air below this temperature and burns more intensely than magnesium. Amalgams are readily formed, as are alloys with zinc,[62] magnesium and aluminium,[63] and manganese,[64] whilst the employment of the metal in alloys for flints in pocket petrol lighters is too well known to require repetition. As the " standard " alloy with La, Pr, Nd, etc., and Fe, the metal is added to iron and steel in refining processes to aid the transference of N, O, P, S, etc., from the metal to the slag. Cerium is also stated to increase the toughness of aluminium by decreasing the effect of the silicon present.[65] The efficiency of the rare earths as catalysts has, of recent years, attracted much attention on their substitution for other less sensitive or less efficient materials, and here again, on grounds of abundancy, cerium oxides have been the most thoroughly investigated. One of the earliest applications was the use of CeO_2 in the Welsbach gas mantle, and further investigation has shown[66] that the catalytic nature of the rare earths has been found to function in several different types of reactions, oxidation, reduction, compound formation, etc., and not only are they effective alone, but also, when used as " promoters," contribute to the activity and length of life of other catalysts.

Praseodymium.—This and neodymium were the two constituents separated from the old didymium of the last century. According to the formation of Pr_2O_3 and PrO_2, the element may be considered both ter- and tetra-valent, the dioxide being prepared from the element by heating in air, and the lower oxide formed by reduction of PrO_2 by hydrogen at 900° C. The dioxide is weakly basic, but corresponding salts have not so far been obtained. Holleck, however, claims that the *bi*-valent sulphate can be obtained under suitable conditions, but is unstable and readily oxidised.[67] The halogen salts are simple of preparation, but the sulphide, like those of Ce, can be prepared only by the passage of H_2S over the heated sulphate. On heating the sulphide it is readily converted to the oxy-compound Pr_2O_2S. The sulphate, basic sulphate, and acid sulphate are known, with the respective formulæ $Pr_2(SO_4)_3$, $(PrO)_2 SO_4$ and $PrH_3(SO_4)_3$, whilst the normal sulphate also forms soluble double salts with alkali sulphates. Many so-called didymium salts have been prepared,[7] but these cannot be regarded as strictly analogous to the praseodymium compounds.

Metallic praseodymium may be obtained by electrolysis of the fused chloride, but apart from its

58 Appleton and Selwood. *J. Am. Chem. Soc.*, **63**, 2029, 1941.
59 Mitchell and Ward. "Modern Methods of Quantitative Analysis." London, 1932.

60 *J. Chem. Soc.*, **110**, ii, 35, 1916.
61 Guillet. *Rev. metall.*, **19**, 352, 1922.
62 Schram. *Z. metallkunde.*, **33**, 558, 1941.
63 Bolmer and Choulart. *ibid.*, **33**, 394, 1941.
64 Jan and Hoffmann. *ibid.*, **33**, 361, 1941 ; Mader and Lawes. *Aluminium*, **25**, 197, 1943.
65 David. METALLURGIA, **28**, 264, 1943.
66 Hopkins and Taebel. *Tr. Electrochem. Soc.*, **71**, 45, 1937.
67 *Atti. X° congr. intern. chem.*, **2**, 671, 1938.

employment as a catalyst promoter, and in the pyrophoric alloy of lighter flints, it has little industrial use and few alloys of praseodymium have been prepared.

Neodymium.—Although this element might be called the twin of praseodymium, some characteristics of the two elements differ. The formation of the two praseodymium oxides is not mirrored in neodymium, which, when pure, forms only the sesquioxide. In the presence of traces of Ce and Pr oxides, however, a dioxide is claimed to have been observed,[68] halogen salts are known, particularly the chloride. The sulphide is formed in the same way as Pr_2S_3, but does not give an oxysulphide when heated. Sulphates and other salts are known as for praseodymium, and the metal is obtained in the same way as that element, as a faintly yellow substance which is moderately stable in air, but gradually becomes covered by a film of greyish oxide. It is attacked slowly by water in the cold, but with heating the reaction becomes more rapid.

Element No. 61 (Illinium).—Apart from the characteristics assigned to this element by Moseley's interpretation of the Periodic law,[69] little is known of this member of the rare earth group, and so far the element has not been obtained as such : indeed, by some authorities, its very existence is queried, but the bulk of evidence is for the identity of this substance as the missing link in the rare earth chain.

Samarium.—The classic investigations of Cleve on this subject were somewhat vitiated by the impurity of his compounds, and unfortunately since this point of error was pointed out, little work has been accomplished on this element, although Martignan and his colleagues did carry out a certain amount of work on the pure salts. Samarium is prepared by electrolysis of a molten mixture of the anhydrous chloride with $BaCl_2$, as a greyish white metal, slowly oxidised in air to Sm_2O_3, a white powder with a faint yellowish tinge, which does not form higher oxides when heated in air. In addition to salts corresponding to this trivalent oxide, the element also forms halides of the form SmX_2, which are, however, relatively unstable. The salts in general exhibit the characteristics exemplifying the cerium group metals ; the halogen trivalent salts are known and well defined, and the sulphide is obtained by heating $Sm_2(SO_4)_3$ in H_2S, or SmC_2 in sulphur vapour. A basic sulphate is obtained by heating the normal sulphate, and an acid sulphate is also known. Many other inorganic and organic salts have also been variously described.

Europium.—This element has been justly called the rare, rare earth element, and very little is known of its compounds or their properties. Both di- and tri-valent salts may be obtained if one be guided by the preparation of the two chlorides $EuCl_3$ and $EuCl_2$; the divalent salt being obtained from the trichloride by reduction with hydrogen at 270° C. ([70]) ; it is relatively unstable, but less so that $SmCl_2$. The work of McCoy appears to confirm the bivalency of the element.[71] Several organic salts have been obtained by James and Robinson,[72] whilst Hopkins and Taebel have reviewed the chemistry of this element in particular.[73]

Gadolinium.—In common with the other elements of the terbium family, this element is tervalent and forms

an oxide of the form R_2O_3, which when pure is white, although the common presence of terbia causes the powder to assume a yellowish colour. Gd_2O_3, like the hydroxide $Gd(OH)_3$, is strongly basic and rapidly absorbs CO_2 to give the carbonate. The characteristics of the salts call for no special comment, but according to Klemm and Bommer,[74] gadolinium is the only ferromagnetic metal amongst the rare earths, although adjacent elements show transition from para- to ferromagnetism. There is also evidence for the bivalency of the element.[75]

Terbium.—The main drawback which hindered study of this element was the difficulty of ensuring complete freedom from gadolinium and neighbouring elements. When once the pure oxide had been obtained, however, several salts, of the type RX_3 and organic compounds were prepared and examined. As well as the white sesquioxide, a black peroxide Tb_4O_7 is obtained by ignition of the oxalate. The composition of this peroxide is still a matter of doubt, as the questions of salt formation and admixture of TbO_2 have not yet been settled.

Dysprosium.—The salts of this element have a more or less pronounced yellow colour, but the oxide Dy_2O_3 is a pure white powder which, as shown by Urbain and confirmed by Jantsch and Weisenberg,[76] produces no higher oxide by heating in oxygen or air at 300°–1,000° C. From the chloride, an oxysalt DyOCl may be obtained by heating in oxygen, and other salts show similarity in general with those of the other rare earth metals.

Holmium.—The doubt which until recently surrounded the individuality of this element may now be assumed to have been disseminated. The conflicting results which have been obtained by various workers can no doubt be attributed to the employment of impure compounds for general investigations, and particularly for the determination of the atomic weight. The oxide Ho_2O_3 is of pale yellow colour and dissolves in acids to produce yellow to orange-coloured solutions. Little is known specifically of the salts, although the chloride and sulphate have been prepared in quantities sufficient for further investigation, and several other salts, inorganic and organic, are known.

Erbium.—This element, too, at one time occasioned doubt as to its homogeneity, and its acceptance in 1910 as an element in its own right was due to the work of Hoffmann and his pupils.[77] The oxide and salts of the elements are rose-coloured compounds, the platinocyanide showing also a green fluorescence. The oxalate, when heated yields the oxide, but this latter retains considerable amounts of CO_2, which for the best work must be removed ; the author has found that the presence of $Gd(OH)_3$ in the desiccating chamber rapidly effects this purification. The preparation of the oxide from the sulphate by ignition takes place via the dioxysalt $Er_2O_3.SO_2$ or $Er_2O_2(SO_4)$, which appears at 845° C., complete conversion being reached only at 1,055° C. A few organic compounds have also been prepared.

Thulium.—The dissension on the identity of this element was subdued when in 1911 James described the chloride, bromate, sulphate, nitrate, oxalate, acetylacetonate and phenoxyacetate of the metal. The oxide is a dense white powder with a greenish tinge, which when heated to incandescence emits a carmine-coloured glow. The salts have a greenish tint which the presence of

68 Brauner. *Z. Anorg. Chem.,* **32**, 1, 1902.
69 *Phil. Mag.,* **27**, 709, 1914.
70 Jantsch, Skallis and Grubitsch. *Z. Anorg. Chem.,* **216**, 75, 1933.
71 *J. Am. Chem. Soc.,* **58**, 1577, 1936.
72 *ibid.,* **35**, 754, 1913.
73 *Tr. Illin. State Acad. Sci.,* **32**, 132, 1939.

74 *Z. Anorg. Chem.,* **231**, 138, 1937.

erbium changes progressively to pink. The properties of the salts are similar to those of the other rare earths, and Holleck and others[75, 67] suggest that bivalent forms might exist.

Ytterbium and Lutecium.—Little is known of the chemistry of these two elements. The oxides, of the form R_2O_3, are white powders in which the presence of traces of thulium produce a brown colouration. The chlorides, sulphates, nitrates, carbonates, oxalates and platinocyanides of the "old" ytterbium (Yb + Lu) were prepared by the earlier workers and when the complexity of Marignac's ytterbium was confirmed and the two constituent elements separated, it was found that the characteristics of the old substance were applicable in almost every way to the new metals. With these elements also, recent work has indicated the probable presence of bi-valent compounds.[75]

Methods of Determination and Identification

In common with the generally accepted methods of identification of most inorganic cations, detection of the rare earths can be accomplished by use of the spectrograph, and in addition, several methods have been proposed for their determination by this means.[78] As will be seen from Table IV, however, approximately half of the rare earths show persistent spectra only in

TABLE IV.

Element.	λ of Persistent Spectra.	Element.	λ of Persistent Spectra.
Cerium	4012·4 Å 4040·76 4165·61 4186·6	Dysprosium	4000·50 Å 4046·00 4077·98 4167·99 4211·74
Praseodymium	4062·83 4179·43 4189·52 4225·34	Holmium	3748·19 3891·02 2936·8
Neodymium	3951·15 4177·34 4303·61	Erbium	3499·12 3692·65 2906·34
Illinium	—	Thulium	3761·92 3761·33 3462·21
Samarium	4390·87 4424·35 4434·34	Ytterbium	3289·37 3694·20 3988·0
Europium	4129·72 4205·03	Lutecium	4518·57 3554·43 3472·48 3397·07 2911·39 2894·85
Gadolinium	3646·19 3768·40		
Terbium	3509·18 3561·75 3848·76 3874·19		

the ultra-violet. This is overcome, however, by examination of the absorption spectra, which method may also be employed to a certain extent when the presence of large amounts of "masking" elements (Na, etc.) renders normal methods unusable. In general examinations of material, where the presence of the rare earths is unsuspected until an incomplete summation is obtained after quantitative analysis by chemical means, it is preferable to carry out examination of the oxalate precipitate to avoid the possibility of masking elements interfering with the persistent lines. Even in this case,

however, some interposition by thorium may be encountered, but this can to a certain extent be avoided by accuracy in technique, etc.

Purely chemical methods of detection and determination of the rare earths are somewhat hindered by our lack of knowledge of their chemistry. Spot tests have, as has been said, provided most of the literature available on the reactions of the rare earths; reference has already been made to Schemjakin's work in this sphere,[36] but others have also contributed. Goswami and Sarkar investigated the triple Cs-Na nitrites of the rare earths,[79] Beck, the use of cacotheline and alizarin –3–sulphonate,[80] whilst general work was conducted by Martini,[81] and specific reactions of the Ce cations were critically reviewed by Wenger and his associates.[82]

Chemical determination has in the main been confined to cerium, advantage being taken of the oxidising propertes of the sulphate.[59, 83] Europium has been determined iodimetrically,[71] but gravimetric methods have enjoyed a wider application than volumetric processes, the general methods of fractional precipitation or electrolysis being applied wherever possible.

Electrometric methods are now being widely applied, and there is little reason to doubt that the use of the polarograph and potentiometer will, within a short time, replace many existing methods of determination.[27, 75, 84]

Two further methods of analysis might be mentioned as of interest, although they may hardly be considered practically applicable. Analysis by artificially induced radioactivity was suggested by Goldschmidt and Djourkovitch,[85] who determined by this means the Dy content of a mixture of rare earths. Thermal analysis of nitrate mixtures was suggested by Quill and his associates[86] for quantitative estimation of the rare earths whose simple and double nitrates form solid solutions with the corresponding rare earths and bismuth salts, reference of the melting-points, etc., being made to a pre-computed liquidus curve.

Conclusion

The outstanding problem presented by the rare earth elements is that of individual separation. Until simpler and more efficient methods of isolation are available, our knowledge of rare earth chemistry in general and in particular will progress but slowly. It is of little avail to work with a 99% pure salt and then report one's findings as of the pure compound.

With enhanced methods of separation, larger quantities of the individual elements will become available for the research into the finer details of rare earth chemistry and structure. It might be argued that it is impossible to attempt refinements in separation processes if no chemical data are available on which to base these refinements. It must be pointed out, however, that as cerium is comparatively plentiful and easily separated, and, generally speaking, embodies in itself the reactions of its congeners, a systematic investigation of the properties of that element would without doubt clarify some aspects of separation processes and technique; and in particular, it is suggested that a concentrated effort

75 Noddack, Brukl and Holleck. *Z. Angew. Chem.*, **50**, 362, 819, 1937.
76 Compt. rendu., **142**, 785, 1906; *Monatsh.*, **68**, 394, 1936.
77 *Ber.*, **43**, 2631, 1910.
78 Boronskii, Troudy, Vsesoyuz. *Konf. Anal. Khim. Akad. Nauk* (S.S.S.R.), **1**, 155, 1939; McCarty *et al. Ind. Eng. Chem.* (Anal.), **10**, 184, 1938; Piccardi. *Spectrachim. Acta*, **1**, 249, 1939; Shinoda. *J. Chem. Soc.*, Japan, **56**, 1483, 1935; *ibid.*, **62**, 529, 1941.

79 *J. Indian Chem. Soc.*, **12**, 608, 1935.
80 *Mikrochim. Acta.*, **3**, 141, 1938; *Microchemie.*, **27**, 47, 1939.
81 *Pub. inst. investig. microquim. Univ. nacl. litoral.* (Rosario, Argentina.) **1**, 71, 1937.
82 Wenger, Duckert and Rusconi. *Helv. Chim. Acta.*, **25**, 1547, 1942.
83 Saitscherbakov. *Zarodsk. Lab.*, **6**, 160, 1937.
84 Jantsch and Gavalovski. *Z. Anal. Chem.*, **107**, 389, 1930; Jantsch. *Osterr. Chem. Ztg.*, **40**, 77, 1937; Atanasiu. *Z. Anal. Chem.*, **113**, 276, 1938; Holleck. *Ibid.*, **116**, 161, 1939; *ibid.*, **126**, 1, 1943.
85 *Bull. Soc. Chim.*, **6**, 718, 1929.
86 Quill, Robey and Seifter. *Ind. Eng. Chem.* (Anal.), **9**, 389, 1937.

on investigation of methods of electrolytic separation would bear fruit.

Identification of the elements will become progressively easier as spectroscopic apparatus and technique acquire enhanced applicability and accuracy, whilst determination of the elements requires only refinement of existing electrochemical analytical processes to ensure the extreme accuracy necessary for an enlightened understanding of the chemistry of the rare earths.

With purer materials, also, the structure of the elements will be rendered more distinct, and our knowledge of atomic and molecular structure brought nearer to completion. On a basis of more efficient separation, therefore, we may proceed to fully characterise the rare earth elements, and indicate some possible industrial applications, rather than trust, as is the general case at present, to rule-of-thumb methods and chance discoveries.

Distortion-free Metallic Hearths

FOR many years furnace engineers have sought to evolve a metallic hearth for heat-treatment, carburising and annealing furnaces, by reason of the many advantages ensuing from the installation of such hearth protection—a metallic surface facilitates charging and discharging operations—hearth temperature is quickly recovered after the charging of a cold load ; and there is a far greater resistance to abrasion than with a brickwork hearth, thereby greatly reducing maintenance charges to the equipment.

in such a manner that the tiles cannot be displaced even when subjected to rough handling.

The design of the small tiles is such that distortion is completely avoided, and a complete hearth can be built up, or dismantled, in a few minutes, so that if after long service a tile should fail, it can be replaced at negligible cost, whereas the failure of any portion of the surface of an ordinary plate hearth means the replacement of the complete large plate. Apart from protecting the hearth itself, the design of the nicrotectile hearth also provides protection for the furnace guard tiles on either side of the hearth, and this additional feature is of the greatest practical value. In most instances the small turn-up along the side and back of the hearth provides ample guard-tile protection, but when required this height can be increased to 12 in. or more by the use of special interlocking vertical side elements.

Patent incandescent " Nicrotectile " furnace hearth fitted into an 8 ft. 0 ins. × 6 ft. 0 ins. heat treatment furnace.

The design of the hearth is clearly indicated in the illustration, which shows how a complete hearth area is covered by a series of special standard interchangeable elements. Special sizes are supplied to complete the dimensions of a standard hearth when necessary, and suitable front locking plates for bolting to the existing furnace cill plates are also provided.

Although originally designed for hearth protection, these tiles can be used for many other purposes, being particularly suitable for the construction of waste gas dampers operating at temperatures up to 1,100° C., their use eliminating in many cases the necessity for water-cooling with all its attendant complications.

Because of such advantages, it has been common practice to fit heat-resisting plates on an ordinary brickwork hearth in furnaces subject to unusually rough and heavy usage, but the general development of this form of hearth protection has been hindered by the relatively high distortion of such plates when they become continually subjected to the loading of cold components. Such distortion not only makes it difficult to charge and discharge the furnaces, but the life of the plates is considerably reduced because the protective scale, normally formed on the surface of a heat-resisting metal, is cracked off when the plate distorts, with the obvious result that oxidation in depth quickly develops.

Designed for use in furnaces operating at temperatures up to 1,000° C., the Patent Incandescent Nicrotectile Hearth* completely eliminates these disadvantages. The complete hearth area is covered by a series of small heat-resisting tiles positively interlocked in all planes

National Certificates in Metallurgy

IT had been expected that the scheme for National Certificates in Metallurgy in which the Iron and Steel Institute, the Institution of Mining and Metallurgy, and the Institute of Metals are co-operating with the Board of Education, would be launched in time to allow colleges and schools to start their courses in the academic year beginning September, 1944.

This has, unfortunately, proved impracticable. The scheme will now come into operation so that courses will begin in September, 1945, and the first examinations will be held in 1946 for the Ordinary Certificate. Colleges and schools are being advised to this effect by the Board of Education, so that as much progress as possible can be made in anticipation.

* Registered trade mark and design No. 625,113 (patents pending).

ORGANIC textbooks, otherwise excellent and up-to-date, frequently contain a section on ultimate analysis in which the methods are so obsolete that one automatically looks, in the illustrations, for operators in knickerbockers, Norfolk sporting jackets, and walrus moustaches. This anomaly in a book which, to instance a recent example, contains a section dealing with the ultra-centrifuge, is, unfortunately, all too common. Presumably, elementary analysis is widely regarded merely as one of the less inspiring side-lines which must, alas, be acquired by the would-be organic chemist. No doubt there are still some chemists who claim with meaning emphasis that the older methods were good enough for them. But the feats that were performed on the penny farthing bicycle are no argument for its survival. It might respectfully be suggested to intending authors of organic text-books that they do one of three things : (1) Leave analysis alone, as being, nowadays, the job of the analyst : (2) learn something about the developments during the past twenty years in analytical practice : or (3) ask an expert to write the section for them. None of these courses will really reflect on the ability of the writer. Any of them will at least be a nearer approach to the greatest good of the greatest number.

Amperometric Titration
Part I—General Considerations
By J. T. Stock, B.Sc., A.R.I.C.

Amperometric titrations are directly derived from polarographic methods, which have been dealt with in a previous article. These titrations have been applied with some success to a variety of inorganic estimations, using both inorganic and organic reagents. They have most of the advantages of the polarographic technique, and can be used to determine extremely small quantities of metallic ions.

DURING the past few years a new method of electrometric titration has been added to our ever-growing armoury of special methods of analysis. The newcomer, though in comparatively early stages of development, may well become very useful. Kolthoff and Pan,[1] in the first of a series of papers dealing with the method, have reviewed the historical aspects and discussed the question of nomenclature. They proposed the name *amperometric* titration, since the method involved the *measurement* of the current flowing between a pair of electrodes immersed in the solution. This terminology is analogous to that employed in the other two important electrometric methods—viz., those of conductiometric and potentiometric titration.

Relation to Polarography

Amperometric titration is generally carried out using the dropping mercury electrode, at which the polarisation effects are accurately reproducible, permitting actual measurement of the current flowing. The technique is accordingly similar to that of polarography. Subsequently, Laitinen and Kolthoff[2] described a rotating

platinum micro-electrode which they showed could be used with advantage in certain cases. Besides these true amperometric procedures, there are others in which the sudden appearance or disappearance of polarisation serves to indicate the end-point, such as the "dead-stop" method of Foulk and Bawden.[3] These will not be considered in the present article.

In the polarographic method of analysis, a dilute, oxygen-free solution of the substance to be estimated is electrolysed, using as one electrode small drops of mercury falling regularly from a glass tube of very fine bore. In nearly all cases a large excess of an "indifferent" or "supporting" electrolyte is added, and sometimes a trace of an agent such as gelatine, to remove irregularities termed "maxima." In most cases, processes of reduction are studied, when the dropping electrode is made the cathode. Generally, on applying a small voltage to the electrodes, little or no current flows, and as the voltage is steadily increased, it is not until the "reduction potential" of the substance is reached that the current begins to rise rapidly with further increase in voltage. Finally, the current ceases to rise further, and remains almost constant with

1 M. Kolthoff and Y. D. Pan. *J. Amer. Chem. Soc*, 1939, **61**, 3402.
2 H. A. Laitinen and I. M. Kolthoff. *J. Phys. Chem.*, 1941, **45**, 1079.

3 C. W. Foulk and A. T. Bawden. *J. Amer. Chem. Soc.*, 1926, **48**, 2045.

further increase in voltage. Only when another electrode reaction sets in, such as the decomposition of the supporting electrolyte, does the current rise rapidly again. If the current flowing is plotted against the corresponding applied voltage, curves of the shape shown in Fig. 1 are obtained. The rising portion is termed a polarographic " wave " or " step." Characteristic of a satisfactory wave is the existence at its summit of a plateau, called the *diffusion current region*, in which the current flowing is almost independent of the applied
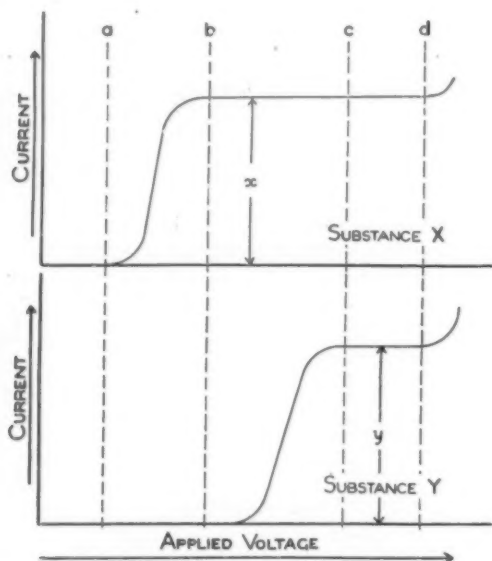

Fig. 1.—Polarographic waves, showing diffusion current regions.

voltage. Thus, in the upper curve shown in Fig. 1, the wave starts at applied voltage a, and the diffusion current region lies between b and d. The magnitude of the diffusion current, or, expressing it in more common terms, the height of the wave, is very often directly proportional to the concentration of the reducible substance. Hence polarographic analysis consists of tracing the current-voltage curve of a solution of the substance in question, and then measuring the wave height (x or y in Fig. 1). From this the concentration of the substance in the test solution is calculated. For further details, an earlier article by the author,[4] and the references quoted in it should be consulted.

Nature of the Results

Consider two substances, X and Y, which separately are soluble, but which mutually precipitate one another when their solutions are mixed. Further, suppose that both substances give rise to polarographic waves, the heights of which are proportional to the respective concentrations. Generally speaking, the two substances will not have identical polarographic characteristics. Thus while X may yield a diffusion current at any applied voltage between b and d, the reduction potential of Y may be higher, so that the diffusion current region is shorter—viz., between c and d.

If a solution of X containing the necessary supporting

electrolyte, etc., and freed from dissolved oxygen, is placed in the polarographic cell, and a voltage between c and d applied, a current proportional to the concentration of X will flow. A solution of Y is added in successive quantities from a burette. The first addition precipitates part of X, reducing its concentration. Accordingly the current falls proportionately. Further additions have a similar effect until, when all of X has been precipitated, the current is zero. On continuing the titration, a new reducible substance Y is introduced into the solution, instead of being promptly removed by precipitation. The current now rises progressively as the titration continues. If the current flowing is plotted against the corresponding volume of titrant, a curve similar to Fig. 2, consisting of two straight lines intersecting in the form of a " V " is obtained. The end-point of the titration is indicated by the point of intersection.

The foregoing description is of an ideal case, and in practice there are several points of difference. The introduction of the titrant unavoidably dilutes the solution, causing the arms of the titration curve to be somewhat curved instead of linear. By making the titrant solution ten or twenty times more concentrated than the test solution, the deviation may be made almost negligible, permitting ready location of the end-point. For precise work, especially in very dilute solutions, the measured values of the current may be corrected by applying a
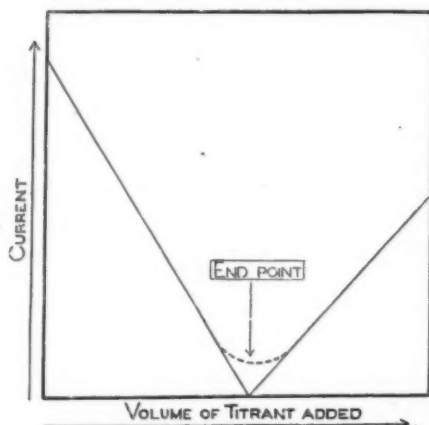
Fig. 2.—Amperometric titration curve, reducible substance titrated with reducible reagent.

simple expression involving the volumes of the test solution and of the titrant added.[5] Using the corrected values of the current, the arms of the titration curve become truly linear. The use of concentrated titrant solutions has the additional advantage that little dissolved oxygen is introduced, so that prolonged bubbling with nitrogen or hydrogen between additions is unnecessary.

Owing to the " residual current " of the solution, due to traces of reducible impurities and to the charging of the steadily falling mercury drops, the current in this type of titration does not fall quite to zero, even with a precipitate of insignificant solubility. In addition to this, a " rounding-off " in the region of the end-point is usually observed, as shown dotted in Fig. 2. This is due to the solubility of the precipitate, but the effect is small unless

4 J. T. Stock. METALLURGIA, 1944, 29 (January), 155.

5 I. M. Kolthoff and J. J. Lingane. *Polarography*, New York, Interscience Publishers, Inc., 1941, pp. 447–78.

the solubility is marked, or when very dilute solutions are being titrated. Unless this curvature is excessive, it is no drawback, since the end-point is located graphically. It is generally sufficient to plot three or four readings either side of the end-point, and to draw through the points a pair of straight lines, the intersection of which indicates the end-point. For precise work, especially when the rounding-off is pronounced, mathematical aids to the location of the end-point have been developed.[6],[7]

Other Varieties of Graph

Suppose that the above titration is repeated, the applied voltage now being reduced to a value slightly in excess of b. Up to the end-point, the current flowing falls as before. At the voltage now being applied, Y yields no wave, and can contribute nothing to the current. Hence the latter does not rise again as the titration is continued, and the resulting titration curve consists of a pair of straight lines intersecting at the end-point, but arranged in the form of a rough " L," as shown in Fig. 3. This is the general shape when the
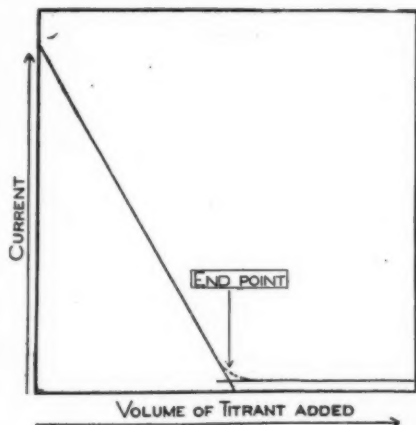

Fig. 3.—Amperometric titration curve, reducible substance titrated with non-reducible reagent.

conditions are such that the substance to be determined is reducible, but not the titrant. If the titrant only is reducible, the current remains small until the end-point. Further addition of titrant causes a progressive rise in current. The titration curve is then of " reversed L " shape.

The two " L " curves show that substances which do not give rise to a polarographic wave under ordinary circumstances may sometimes be determined by titration with a reducible precipitant, or, alternatively, may be used to titrate reducible substances. Thus, the fluoride ion, which gives no polarographic wave, can be titrated with a solution of thorium or lanthanum nitrate.[8] a " reversed L " curve resulting. Especially when much rounding of the curve occurs, location of the end-point is not so precise as in the case of the " V "-shaped curves obtained when both reactants are reducible. In certain instances it is possible to produce a curve consisting of three straight portions, permitting two substances in the same solution to be titrated. [1],[9]

Another type of titration curve is obtained when the substance to be determined yields an *anodic* wave—i.e., when the dropping electrode acts as the anode—while, at the same applied voltage, the titrant yields a cathodic wave. As the titration proceeds, the current decreases to zero, as before. After the end-point the current increases again, *but its direction is reversed*. The titration curve has the appearance of a single line cutting the volume axis at the end-point, as shown in Fig. 4. When it is the titrant which yields the anodic wave, the
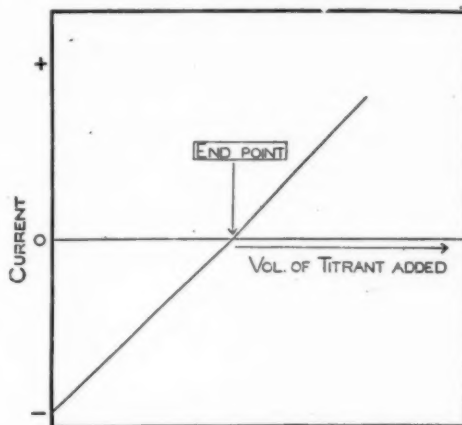
Fig. 4.—Amperometric titration curve when substance to be determined yields an anodic wave.

titration curve slopes in the opposite direction. Generally, the portions of the curve before and after the end-point will not have quite the same slope. Curves of this type were first obtained by Strubl[10] who used titanous chloride solutions (trivalent titanium yields an anodic wave) to titrate oxidising agents, such as ferric iron, chromate and permanganate. The reverse titration— viz., of titanous salts by oxidising agents, was studied by Spalenka.[11] Incidentally, it is interesting to note this reaction involves no precipitate formation, being an instance of oxidation and reduction. Other titrations involving anodic waves are the titration of halides with soluble salts of silver, [12],[13] or of mercury,[5] and of the titration of solutions containing stannous tin with cupric ions.[14]

Miscellaneous Inorganic Titrations

Owing to its many " insoluble " salts, *lead* has featured in several papers. It may be titrated with potassium chromate (or, better, the dichromate) with very accurate results in solutions as dilute as 0·001 M.[1] Either a " V " or a " reversed L " curve results, depending upon the applied voltage. It is even possible to titrate at zero voltage, thus dispensing with the battery and polarising unit.

Lead nitrate solution may be used to titrate certain anions, especially *sulphate*. This titration has not ceased to attract attention since it was first studied by Majer.[15] The curves are of the " reversed L " type, and, since lead

6 I. M. Kolthoff and H. A. Laitinen. *Rec. trav. chim.*, 1940, **59**, 922.
7 A. Langer and D. P. Stevenson. *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 770.
8 A. Langer. *Ind. Eng. Chem., Anal. Ed.*, 1940, **12**, 411.
9 J. T. Stock. *Chem. Products*, 1944, **7**, 23.

10 R. Strubl. *Collection Czechoslovak Chem. Commun.*, 1938, **10**, 475.
11 M. Spalenka. *Collection Czechoslovak Chem. Commun.*, 1939, **11**, 146.
12 I. M. Kolthoff and J. J. Lingane. *Chem. Reviews*, 1939, **24**, 1.
13 O. H. Müller. *J. Chem. Ed.*, 1941, **18**, 320.
14 J. J. Lingane. *J. Amer. Chem. Soc.*, 1943, **65**, 866.
15 V. Majer. *Z. Elektrochem.*, 1936, **42**, 120, 123.

sulphate is appreciably soluble in the presence of other salts, considerable rounding of the curve at the end-point occurs, making the location of the latter somewhat difficult. To suppress the solubility, Spalenka[11] added ethyl alcohol to the solution, and Kolthoff and Pan[16] adopted this procedure after extensive study of the titration. Two technical applications have been described —viz., the determination of sulphur in coke after oxidation to the sulphate,[17] and the determination of sulphate in precipitated alumina and in boiler water.[18]

Molybdate may also be determined by titration with lead nitrate solution, according to Thanheiser and Willems.[19] These workers extended the titration to the determination of molybdenum in steel. Unfortunately the iron and various other interfering metals must first be removed.

For the determination of *phosphate*, Neuberger[20] used bismuth oxyperchlorate solution. Kolthoff and Cohn[21] also examined the titration of this anion, since Neuberger's procedure does not give very accurate results. They showed that uranyl acetate was satisfactory as a titrant, even with very dilute solutions of phosphate.

The well-known determination of zinc by means of potassium ferrocyanide solution may be carried out amperometrically.[11] It is, however, necessary to run the zinc solution into the ferrocyanide solution.

Organic Reagents

Many organic substances give rise to well-defined polarographic waves, especially if the solution is maintained at the correct pH value by the use of buffer mixtures. This suggests that some of the specific organic reagents for metals[22] might be useful in amperometric titration. This has already proved to be the case, although, judging from the number of publications, few of these reagents have yet been tried. Neuberger[23] found that copper could be estimated by adding a known excess of a solution of salicylaldoxime, and then titrating with standard copper solution. The same worker[20] described the titration of nickel with dimethylglyoxime, though with very little detail. Kolthoff and Langer[24] studied this titration systematically, and showed that it was capable of yielding results of high accuracy. The work was extended to cover the determination of nickel in steels. The American workers then examined α-nitroso-β-naphthol,[25] and showed that it could be used to titrate copper, cobalt and palladium. Copper may also be titrated with α-benzoinoxime solution,[26] a faintly ammoniacal solution of ammonium chloride being used as supporting electrolyte.

" Oxine " (8-hydroxyquinoline) has been used in the amperometric titration of bismuth,[27] and of zinc, copper and aluminium.[28]

Apart from some preliminary work reported by the author on the use of quinaldinic acid as a titrant for copper, zinc and cadmium,[9] few other reactions of direct metallurgical interest seem to have been described. Two interesting biochemical applications might be

mentioned in conclusion. α-Tocopherol (vitamin E) may be determined by amperometric titration with gold chloride solution,[29] while the titration of picrolonic acid with methylene blue has been used to estimate calcium.[30]

Advantages and Disadvantages

Operating as it does on polarographic principles, amperometric titration has most of the advantages (and some of the disadvantages) of polarography. It is inherently a microchemical method, capable of handling solutions sometimes as dilute as 0·0001 M. Though most of the work so far reported has been carried out using volumes to be titrated of about 50 ml., there is no reason why micro-cells capable of dealing with much smaller volumes should not be used. This will be discussed in a subsequent article. " Foreign " salts, traces of which have to be so carefully guarded against in conductiometric work, may be present, and are in fact usually added. Even though the precipitate may be soluble enough to cause considerable rounding of the titration curves at the end-point, determination is still possible, since the end-point is located graphically. Amperometric titration should therefore prove applicable when methods depending on the recognition of the actual end-point fail. It is sometimes possible to carry out the titration without removing dissolved oxygen, as was practised by some of the continental workers. This permits working in an open beaker, but is not recommended for any but rough work, unless conditions are such that the oxygen wave is not produced.

Since the titration is carried out at a fixed applied voltage, the simplest electrical apparatus suffices. A reliable, sensitive galvanometer is the principal need. Thermostatic control, definitely to be desired in normal polarography, is unnecessary, since the *change* in current, and not its absolute magnitude, is all that is required. For the same reason, the characteristics of the capillary, provided they are suitable, do not affect the result. No recalibration is required should a breakage occur.

The principal disadvantage of the technique is the interference of readily reducible metals, etc., which contribute to the diffusion current and lower the accuracy or, when their concentration is large, make the titration impossible. Co-precipitation problems are also sometimes difficult. As in the case of polarographic technique, continued research should overcome these difficulties. The principle of modifying the general method to suit the particular substance to be examined will certainly apply.

29 L. I. Smith, L. J. Spillane and I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1942, **64**, 646.
30 G. Cohn and I. M. Kolthoff, *J. Biol. Chem.*, 1943, **148**, 711.

Selective Tests for Cadmium

A REAGENT solution to detect 0·1 μ g. of cadmium in the presence of × 5,000 of copper or zinc is prepared as follows[1] :—Dissolve 0·25 g. αα′-dipyridyl and 0·146 g. ferrous sulphate in 50 mls. water add 10 g. potassium iodide, shake for 30 mins., and filter off any precipitate. The clear saturated solution of the Fe(αα′-dipyridyl)$_3$I$_2$ complex containing excess potassium iodide gives a red precipitate (e.g., on spot-paper) with cadmium. Silver and thallium, if present, should first be removed by hydrochloric acid, and lead, mercury, bismuth and tin by ammonium hydroxide.

1 F. Feigl and L. I. Miranda. *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 141.

16 I. M. Kolthoff and Y. D. Pan, *J. Amer. Chem. Soc.*, 1940, **62**, 3332.
17 G. A. Butenko and V. M. Pindas, *Zavodskaya Lab.*, 1940, **9**, 634.
18 W. C. Davies and C. Key, *Industrial Chemist*, 1943, **19**, 167.
19 J. Thanheiser and J. Willems, *Arch. Eisenhüttenw.*, 1939, **13**, 73.
20 A. Neuberger, *Z. anal. Chem.*, 1939, **116**, 1.
21 I. M. Kolthoff and G. Cohn, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 412.
22 R. Belcher and C. E. Spooner, METALLURGIA, 1944, **29** (April), 329; **30** (May), 49.
23 A. Neuberger, *Arch. Eisenhüttenw.*, 1939, **13**, 171.
24 I. M. Kolthoff and A. Langer, *J. Amer. Chem. Soc.*, 1940, **62**, 211.
25 I. M. Kolthoff and A. Langer, *J. Amer. Chem. Soc.*, 1940, **62**, 3172.
26 A. Langer, *Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 283.
27 J. Gillis, J. Eeckhout and G. Standaert, *Meded. Kon. Vlaamsche Acad. Wetensch., Letteren Schoone Kunsten Belgie, Klasse Wetensch.*, 1940, No. 7, 3.
28 A. M. Zan'ko, *Dopovidi Akad. Nauk. U.S.S.R.*, 1940, 27, 32.

The Distribution of Non-Metallic Inclusions in Steel Ingots

ALTHOUGH the behaviour of non-metallic inclusions in steel ingots has repeatedly been investigated both experimentally and theoretically, there is no agreement as to kind and cause of their distribution within the ingot. In the present investigation two ingots of acid steel have been used. One was of a chromium-nickel-molybdenum steel (no composition is given) and weighed 7,000 kg. (over 15,000 lb.) and the other was of a chromium steel (no composition is given, either) and weighed 3,000 kg. (about 6,600 lb.). A large number of micro-sections have been prepared in various spots of the ingots, and the number N of non-metallic inclusions well visible at a magnification of 600 (i.e., those the radius of which was 10^{-4} cm. or larger) on 1 sq. mm. (0·0016 sq. in.) of the section has been noted. The approximate radius r of every inclusion has been measured as well, and the percentage given of inclusions having radii of 1×10^{-4} cm. 2×10^{-4} cm., etc., up to 14×10^{-4} cm. From these values and the numbers N the relative area A occupied by all inclusions on a micro-section has been calculated.

The main results referring to the relative area A are summarised in the accompanying drawing. It represents one half of a vertical section through the axis of the 7,000 kg. ingot. The curved lines connect points of equal A values, and the corresponding figures for A (in %) are marked at the lines. To check the correctness of these values the amounts of sulphides and silicates in three points of the ingot have been determined by a chemical analysis, and their sum was found to agree (within 15%) with the corresponding A values.

It is seen that the relation between A and the distance D of a point from the surface of the ingot has a rather complicated shape, with a minimum and one or two maxima. On the other

B. I. Gulyaev: *Izvestia Akademii Nauk U.S.S.R. Technical Sciences*, 1942, No. 3-4, pp. 57-75.
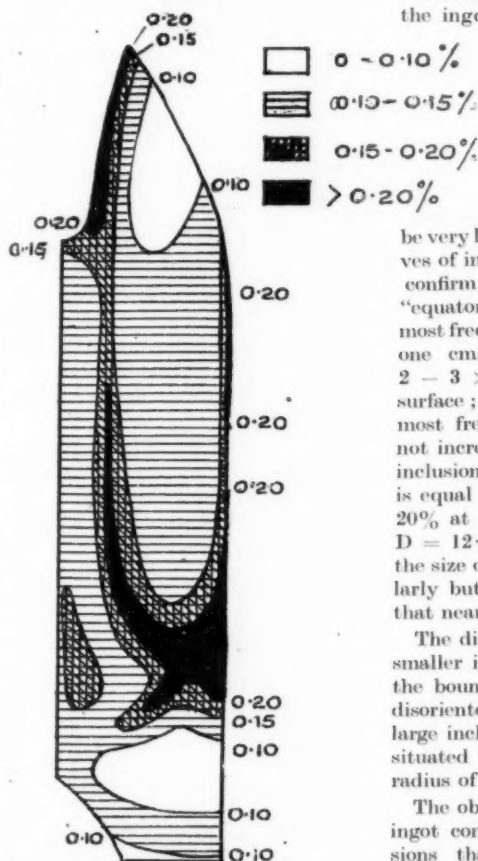
Fig. 1.—The distribution of non-metallic inclusions in steel ingots.

hand, the relation between D and N is very simple. The number of inclusions decreases in a regular fashion when D increases from nothing to about 8 — 11 cm., the radius of the ingot being about 40 cm.; it is nearly constant for D values ranging between 11 and 40 cm. or, in other words, N does not vary within the inner core of the ingot, which core forms a cylinder with a radius of about 29 cm.

The layer which is distant from the surface by 8 — 11 cm., is also the layer of a maximum A (see Fig. 1). It forms also the boundary between the columnar crystals at the outside and the disoriented crystals in the core of the ingot.

Since the number N of inclusions within this layer is only a fraction of that near the surface (e.g., 30 instead of 200), whereas the area A passes through a maximum, the area of an average inclusion must be very large here. The frequency curves of inclusions having various radii r confirm this conclusion. Along the "equator plane" of the large ingot the most frequent radius was 1×10^{-4} cm. one cm. beneath the surface, and $2 - 3 \times 10^{-4}$ cm., 4·8 cm. from the surface; deeper still, although the most frequent size of inclusion does not increase regularly, the number of inclusions over 6×10^{-4} cm. does; it is equal to nothing at D = 4·8 cm., 20% at D = 8·6 cm., and 30% at D = 12·4 cm. At larger values of D the size of the inclusions varies irregularly but always remains larger than that near the surface.

The distribution of radii within the smaller ingot is very similar, though the boundary between columnar and disoriented regions and the layer of large inclusions and large A values is situated 7 — 8 cm. from the surface, radius of the ingot being 29·5 cm.

The observation that the core of an ingot contains less, but larger inclusions than the zone of columnar crystals, makes it probable that each of these larger inclusions originated by a combination of several small particles, i.e., by coagulation. The core of the ingot remains liquid for a longer time than the zone of columnar crystals does, and droplets of non-metallic impurities have more time to meet each other and to coalesce to a larger droplet. The bigger the ingot the more time there is for coagulation, and a mathematical analysis shows that, in the core, the average radius of an inclusion should be proportional to $R^{2/3}$, R being the radius of a cylindrical ingot.

From the results of the mathematical analysis the absolute rate of coagulation can be calculated. It proves to be so high that it cannot be accounted for by ordinary diffusion (Smoluchowsky's theory of coagulation) ; it is evidently much accelerated by convection currents and by stirring due to the operation of casting. The accumulation of large inclusions near the boundary of the columnar zone is due to a special kind of convection.

The mechanical qualities of cast steel, especially the maximum necking at the rupture and the impact strength, are naturally lowered by non-metallic inclusions. A comparison of these qualities with the values of N, A, and r on the nearest micro-sections leaves the impression that r is more important than either A or N. The unfavourable effect of inclusions is the less important the smaller the inclusions are and the more uniformly they are distributed. It might be advisable, therefore, to cast smaller ingots and use a relatively low temperature, so as to give the coagulation as little time as possible.

The paper also contains a new theory of the formation of columnar crystals.

sq. in. Redrawing tests showed that as many as four redraws could be made without intermediate annealings and with at least 95% recovery. It appeared, therefore, that zinc-titanium alloys did not work-harden, as is found with zinc-copper alloys.

The zinc-titanium alloy was also found not to grow excessively large grains when annealed up to 400° C. for periods up to 24 hours. The ductility and other properties were not harmed by annealing and the high creep resistance noted in the hot-rolled alloy, which was sharply reduced by cold-working, was found to be largely restored by suitable heat-treatment. Annealing experiments involving a range of times and temperatures, indicated that much larger, improvements in creep resistance were possible by the use of lower annealing

Rolled Zinc-Titanium Alloys

By E. A. Anderson, E. J. Royle and P. W. Ramsey

ZINC-RICH alloys in commercial use depend largely on solid solution effects for their desirable properties, and typical examples are rolled alloys containing about 1% of copper, with or without additions of elements such as magnesium, and the die-casting alloys, containing about 4% of aluminium, with small amounts of magnesium and sometimes copper. A number of elements are capable of forming alloys with zinc, which do not enter into solid solution except to a limited extent, and the present investigation deals with one such system, zinc-titanium, in which alloys having potentially useful properties in the rolled form were found.

Three alloys were prepared from high-purity zinc (99·99%) and high-purity titanium (98·9%), containing 0·05, 0·12, and 0·23% of titanium respectively. Slab cross sections of the alloys showed a marked grain refinement in the two alloys of high titanium content, and the alloy of low titanium content showed the columnar grain structure of zinc but with a scatter of small equiaxed grains at the centre. The three slabs were hot-rolled to a 0·02 in. in a 12 in. diameter mill with a final coil temperature of about 200° C. The bars rolled easily and produced strip of good surface quality. In Table 1 are given the composition, mechanical properties and inverse creep rates of the three alloys together with similar data for a typical solid solution type alloy containing 99% zinc, 1% copper.

When the inverse creep rates are plotted against stress on a logarithmic basis for a typical zinc-titanium alloy

and the 1% copper alloy, a striking difference was found in the slope of the curves. This difference was inherent, as all the zinc-titanium alloys tested, as well as a series of zinc-iron alloys, gave parallel curves, while several alloys of the solid solution type, zinc-cadmium, zinc-copper, zinc-manganese, etc., gave curves essentially parallel to that obtained for the 1% copper alloy. The effect of the difference of the slope of the curve is to place the zinc-titanium alloys in a position of superior creep resistance as the stress is decreased.

To permit a wider range of conditions of rolling and heat treatment to be considered further tests were carried out with the 0·12% titanium alloy which fabricated well and had drawing properties which only fell slightly short of commercial zinc alloys. It was found that a final 50% cold-rolling would cause sufficiently better drawing properties to make the alloy of commercial interest. Tests on rolling conditions showed that cold-rolling effected a softening and weakening, as compared with hot-rolling. The scleroscope hardness dropped from 21 to 15 and the tensile strength decreased by approximately 1 ton per

TABLE I.—COMPOSITION, MECHANICAL PROPERTIES AND INVERSE CREEP RATES FOR HOT-ROLLED ZINC TITANIUM ALLOYS AND 1% COPPER ZINC.

Titanium, % Zinc Balance.	Gauge, In.	Tensile Strength, Tons per Sq. In.		Elongation, % on 2 in.		Scleroscope Hardness.	Inverse Creep Rates, Days, % Elong. with Grain Stress.		
		With Grain.	Across Grain.	With Grain.	Across Grain.		8,000 lb. per Sq. In.	12,000 lb. per Sq. In.	15,000 lb per Sq. In.
0·05	0·023	8·7	12·3	33·2	13·3	19	24·8	0·055	0·0039
0·12	0·021	9·0	13·3	29·5	12·0	20	190·0	1·05	0·023
0·23	0·022	9·5	13·4	28·3	11·3	22	1120·0	4·66	0·077
1% Cu	0·018	10·6	13·4	35·0	8·7	17	1·95	0·16	No Test

TABLE II.

CREEP AND AGEING TESTS AT ELEVATED TEMPERATURE ON 0·12% ZINC TITANIUM ALLOYS.

Ageing Treatment.	Inverse Creep Rates, Days, %.	
	Test at 25° C. 12,000 lb. per Sq. In.	Test at 150° C. 3,000 lb. per Sq. In.
None	0·36	4·75
1,000 hours at 150° C.	0·52	5·74
1,900 hours at 100° C.	0·62	4·91
1 year at room temperature...	0·23	5·40

temperatures. To test the changes due to annealing, specimens representing actual fabricated material of zinc-titanium alloy, creep tests were made on samples cut from drawn cups. The inverse creep rate in days per cent. increased from 4·2 for the draws material to 140 for material annealed for 5 minutes at 275° C. Similar values for a 1% copper-zinc alloy were 0·18 and 2·2.

Creep and ageing tests at elevated temperatures on the 0·12% titanium-zinc alloy are given in Table 2. Further tests under service conditions are being carried out on cold-rolled strip, annealed at 275° C. for 5 minutes and tested at 3,000 lb. per sq. in. stress at 150° C.

Effect of Hardness on the Machinability of Alloy Steels

By O. W. Boston and L. V. Colwell

THE correllation of machinability with hardness, the sensitivity of machinability to hardness particularly in the high hardness ranges and the relative machinability ratings of six alloys in the quenched and tempered condition were studied by means of a series of turning tool-life tests. The composition of the steels tested together with their grain size are given in Table I. Tests were carried out on bars $1\frac{7}{8}$ inches in diameter and 30 ins. long, oil quenched from 830°C. and tempered to yield nominal hardnesses of 250, 300, 350, 400, 450, and 500 Brinell. Two sizes of cut representing typical rough and finish turning cuts such as might be made with a turret lathe were taken so as to simulate commercial practice. The heavy or rough turning cut was 0·050 ins. deep with a feed of 0·0127 ins. per revolution and the light or finish turning cut was 0·0125 ins. deep with the same feed.

The first group of tests involving heavy cuts with a cutting fluid indicates that, for general machining purposes, the S.A.E. 4340 steel has the highest cutting speed such as V_{10}, of all the six steels tested, this being particularly true at hardnesses below 400 Brinell. The S.A.E. 4145 steel approaches the 4340 steel at high hardnesses, but it could not be machined with consistent results at hardnesses of 450 Brinell or higher, while the latter steel displayed remarkable consistency, even at very low turning speeds necessitated by the hardnesses above 400 Brinell. The second group of tests involving light cuts shows the S.A.E. 4645 steel to have the highest machinability rating, such as V_{10}, except for the difficulty likely to result from poor hardenability. These tests gave a chip formation somewhat different from that of the first group as it is a proportionally thicker chip, similar to those obtained in threading operations.

One of the prerequisites for good machinability in the high hardness range, that is, greater than 400 Brinell, is that the steels possess a high degree of hardenability or uniform hardness penetration. This is evident from the fact that both groups of machinability tests show that the cutting speed for a given tool life may be reduced 15% for approximately 5% increase in Brinell hardness. A steel possessing good hardenability is therefore necessary to avoid pronounced variation in hardness about the periphery, along the axis, and radially, arising from variable factors in heat treating practice. It follows that the S.A.E. 4340 and 4145 steels, which possess good hardenability, should also have superior machining ratings in commercial practice when compared with the other four types of steel.

This applies, however, only to the quenched and tempered condition which usually involves hardnesses considerably higher than those of annealed steels.

The cutting speed, V_{10}, was different, for some of the steels for the low hardness values obtained by annealing, from that of the same hardness obtained by quenching and tempering. Annealed bars of steels S.A.E. 3145 (modified), S.A.E. 5145, S.A.E. 4145, and G.M.C. X3045 A gave cutting cutting speeds (V_{10} and V_{300}) considerably higher than would be obtained for the quenched and tempered bars from heavy cuts. The cutting speed, V_{10}, for the S.A.E. (modified) steel and the S.A.E. 4645 steel was more nearly equal for the same hardness, as obtained by annealing and by quenching and tempering.

TABLE I.—COMPOSITION AND GRAIN SIZE OF STEELS TESTED.

Steel.	Composition.								McQuaid Ehn Grain Size.
	C.	Mn.	Si.	S.	P.	Ni.	Cr.	Mo.	
S.A.E. 3145 (modified)	0·45	0·76	0·23	0·022	0·018	1·27	0·59	—	7
S.A.E. 4645	0·47	0·73	0·21	0·020	0·018	1·82	—	0·25	7
S.A.E. 4340 (modified). Heat 1	0·48	0·66	0·25	0·015	0·017	1·72	0·76	0·21	7–6
S.A.E. 4340 (modified). Heat 2	0·42	0·77	0·21	—	—	1·77	0·75	0·23	—
S.A.E. 4145	0·46	0·78	—	0·020	0·018	—	0·98	0·22	6
S.A.E. 5145	0·47	0·76	0·22	0·023	0·018	—	0·90	—	7
G.M.C. X3045A. Heat 1	0·46	0·83	0·25	0·021	0·019	0·72	0·72	—	6
G.M.C. X3045A. Heat 2	0·48	0·93	0·21	—	—	0·72	0·70	—	—

Effect of Cooling Rate and Minor Constituents on the Rupture Properties of Copper at 200° C.

By D. L. Martin and E. R. Parker

PREVIOUS investigations have shown that the rate of cooling from the annealing temperature prior to testing greatly influenced the life of copper under sustained load at 200° C., and that furnace-cooled bars of oxygen-free copper (with and without silver) had a life four to twenty times that of water-quenched specimens. The addition of 0·054% silver to the oxygen-free copper increased the life at a stress of 10 tons per sq. in. from about 2 hours to 50 hours.

To investigate still further the effect of cooling rate and minor constituents on the rupture properties of copper, two groups of material were tested, one consisting of a wide variety of commercial coppers, and the other composed of special high-purity, laboratory-prepared coppers. The commercial materials were tested to determine whether or not the effect of cooling rate occurred with all coppers, whereas the high-purity coppers were investigated to determine a basis for evaluating the effects of minor constituents on the rupture properties. All the coppers were tested in air at 200° C. in a vertical rupture furnace by subjecting test bars to various constant loads and measuring the time required for fracture. Test specimens were annealed at 850° C. for one hour in a purified nitrogen atmosphere except the high-purity

TABLE I—COMPARISON OF THE 200° C. RUPTURE PROPERTIES OF COPPER.

Copper.	Treatment.	10.7 Tons per Sq. In.			10 Tons per Sq. In.			8.9 Tons per Sq. In.			8 Tons per Sq. In.		
		Hours.	Elong. % on 1 in.	Red. of Area, %.	Hours.	Elong. % on 1 in.	Red. of Area, %.	Hours.	Elong. % on 1 in.	Red. of Area, %.	Hours.	Elong. % on 1 in.	Red. of Area, %.
Commercial oxygen free	F.C.	2.5	26	43	5.5	24	40	28	21	37	100	19	34
	W.Q.	0.7	27	38	1.0	25	36	5	21	28	18	18	23
Commercial silver bearing oxygen free	F.C.	2.5	33	48	11	29	44	380	22	36	1,000	20	34
	W.Q.	0.5	35	53	2.5	30	44	50	23	32	600	18	24
Tough pitch (low impurity)	F.C.	0.2	75	71	1.0	56	70	10	38	43	30	31	34
	W.Q.	0.2	58	68	1.0	43	49	3	36	39	10	29	31
Tough pitch (high impurity)	F.C.	0.5	53	54	2.5	43	47	10	36	39	40	30	34
	W.Q.	0.2	46	47	0.6	39	41	3	30	33	15	24	27
Silver bearing tough pitch	F.C.	15	56	69	80	54	63	1,000	50	55	1,000	—	—
	W.Q.	4.5	49	57	30	45	43	300	40	30	1,000	—	—
Commercial coalesced oxygen free	F.C.	0.3	32	47	0.8	27	37	2	22	29	5	19	23
	W.Q.	0.3	28	47	0.8	23	36	2	20	27	4	17	22
Synthetic copper oxygen free	F.C.	7.0	35	48	16	30	40	60	25	30	220	21	24
	W.Q.	0.3	30	—	0.6	25	—	2.5	21	—	8	17	20
High purity, oxygen free	F.C.	0.4	19	42	0.9	18	38	2.8	16	33	9	14	29
	W.Q.	0.1	—	63	0.2	—	50	0.6	—	35	1.7	—	26

copper which was heated in vacuum, and half of the specimens were cooled in the furnace at approximately 100° C. per hour, and half were water-quenched. The heat-treated bars were tested by suspending them with long extension rods in the hot zone of the rupture furnace. A summary of the rupture-tests results are given in Table I, where the values for life, elongation and reduction of area are tabulated for various stresses.

The effect of minor constituents on the rupture properties is difficult to evaluate exactly because the part played by other variables, such as grain size, is not completely understood. An addition, however, of 0.012% of soluble elements to the high-purity copper is sufficient to increase the life twenty-fold. The increased resistance to fracture of an oxygen-free copper containing soluble impurities appears to be related to the higher softening temperature, although the effect is partly due to the smaller grain of the impure copper. The presence of oxygen in the copper introduces other factors and furnace-cooled oxygen-bearing copper was found to have a shorter life in rupture (at the same stress) than oxygen-free copper of the same general composition.

The role of oxygen in reducing the the life of an alloy copper appears to be one of purification of the copper matrix. In a furnace-cooled tough-pitch copper some impurities exist primarily as oxides, leaving a purer copper matrix of lower resistance to rupture than copper containing dissolved elements. Water quenching on the other hand, retains the elements in solution, so that very little difference exists between the life of quenched oxygen-bearing and quenched oxygen-free copper of the same general analysis. The net effect of oxygen in an impure copper is to decrease the effect of cooling rate on the life under sustained loads.

The results show that great changes in the rupture life of copper at 200° C. are caused by varying the rate of cooling from the annealing temperature. Specifically, the faster the cooling rate, the shorter the life and the lower the ductility. The effect was found for a wide variety of coppers, including spectrographically pure copper, 99.999 + % pure.

The experimental data obtained in the cooling experiments are explained by the hypothesis that attributes the effect of cooling rate to variations in the degree of perfection of the atomic arrangements. Water quenching retains imperfections in the lattice which are generated at high temperatures by thermal fluctuation, and furnace cooling permits the atoms to become more perfectly arranged with fewer lattice imperfections. Such imperfections or dislocations are assumed to be responsible for the weakness of metal crystals, and consequently the material containing the greatest number of free dislocations should have the shorter life, i.e., the water-quenched copper. Variations in the rate of cooling from the annealing temperature also influenced the creep characteristics and the internal friction of the copper.

Small degrees of cold work prior to testing were found to decrease the rupture life of furnace-cooled copper. Beyond a certain degree of deformation, however, the life was increased by cold stretching which confirmed the work of previous investigations on

"strain-weakening" and showed that plastic deformation does not always increase the resistance of a metal to further deformation, but may actually produce a condition more favourable for slip.

Planned Grain Flow in Forgings

By W. Naujoks

THE phenomenon of grain flow, or flow-lines, in wrought materials, particularly in forgings of iron and steel has always been associated with the strength and toughness of these forgings, but for a long time there has been no satisfactory understanding or explanation as to the actual developments of flow-lines in wrought materials, nor has there been any logical conception as to the function they served. Developments in engineering have increased the variety of shapes to be forged and led to the discovery that in forged parts increased strength and toughness could be obtained without a corresponding increase in weight by positioning the flow-lines in relation to the stress direction.

The inception and development of flow-lines in the wrought metals is the product of two actions, one chemical and the other mechanical. Even in the highest grades of steel of a given composition some impurities remain in the form of inclusions which are present between the grain boundaries and are weaker generally than the metal grains, particularly when the inclusions are oxides or silicates. During a series of cogging and rolling

operations, inclusions are drawn out and do not revert to their original shape when the finishing temperature is reached, since they are not affected by heating or cooling in the manner that steel crystals are. The result is the fibre structure in wrought materials. Non-ferrous metals contain similar inclusions and offer similar properties in wrought and forged parts.

The position of the flow-lines in forgings depends upon the positioning of the forging stock in the initial forging operation and upon the design of the subsequent sequence of forging steps in flowing the metal to the final shape. The forging stock can be placed in between the forging dies, so that the flow-lines in the forging stock are horizontal with the dies, that is, parallel with the die faces. In the horizontal position the flow-lines may be positioned parallel to the length of the dies, or at right angles to the length, or at some desired angle in between. The forging stock may also be set up-end on the dies, so that the flow-lines are in a vertical position. The exact initial positioning and the subsequent forging operations depend upon the shape and complexity of the forged parts and upon the direction of the important stresses on the part when in service.

In general practice, grain flow position is specified after a stress diagram has been made, and this practice is now used to determine grain flow position for all important aeroplane parts, including motor parts, fuselage fittings, landing gear forgings, and other highly important aircraft forgings

Continuous Casting

By T. W. Lippert

ALTHOUGH continuous casting has been practised for about a hundred years it is only during recent years that rapid progress has been made in its development. To-day commercial technique has been developed to permit one of the many continuous casting processes to be applied to a wide range of ferrous and non-ferrous metals. A symposium on the subject was recently held by the American Institute of Mining and Metallurgical Engineers, at which several papers were presented.[1] The present position of the whole field of continuous casting technique was surveyed by T. W. Lippert[2], who introduced the symposium.

The subject is introduced by a brief historical survey which is followed by notes on recent developments and the present position of thirteen continuous casting processes, the more important of these being subsequently discussed at considerable length. Reference is made to the following processes : Hazelett, Yunghano-Rossi, Merle, Poland-Eldred, Alcoa D.C., Williams, Goss, Hopkins, Dow, Reynolds, Inco, Soro, and Pluramelt. The equipment and technique devised for these processes and a scattering of little-known or unknown contemporaries, all fit within the framework of ideas propounded by a long line of predecessors. The past few years, however, have brought forth several unique and unorthodox machines and methods. One of these is best known as Alleghany-Ludlum's Pluramelt process, conceived by R. K. Hopkins, of M. W. Kellog Co. ; and the other is the Soro process, invented by the Swiss, Edwin Schuetz, and employed commercially in several countries.

The Pluramelt process is a type of continuous casting process which is used more particularly to build up special alloy steel facings on carbon steel ingots, the facing being cast in the space between the ingot and a refractory mould. All the constituents of the steel are fed in powdered form in suitable proportions down tubes to the working head which operates under a slag blanket. The head is made up of a number of carbon steel tubes which also function as electrodes, the result being a multiple arc-furnace. There is practically no limit to the complexity of alloy constituents that can be metered into the system at one time. Steel made in this way is very uniform, furthermore, many analyses can be so produced that are difficult or almost impossible of production by conventional refining and metalworking methods.

The Soro process is not, strictly speaking, a continuous process ; briefly, it consists in the centrifugal casting of a ring or circular or other cross section in readily demountable iron moulds. These are arranged for simultaneous casting of two rings. After casting, the mould is opened and the rings removed. The moulds are then cleaned, a wash is applied, and they are assembled for the next cast. In operation a cast can be made every minute or so. The cast rings then go to a milling machine, which removes the pouring burr on the internal diameter of the rings, into which burr is concentrated, the sinkhead or pipe and all chemical segregates associated therewith. A correctly profiled ring of metal is obtained which is cut at one point with a small metal saw. The two ends are then spread sufficiently apart using an eccentric press to permit one end to be entered into a straightening device attached to a draw bench. Various methods of drawing and straightening can be used.

There is an interesting aspect of this invention which is presented by the author in the following manner :

" While for almost four centuries the poets have belabored the phrase that ' necessity is the mother of invention,' there is no gainsaying the fact that anger can be an equally effective stimulant to the inventive Muse. Armed with righteous anger and a wad of the plant ' know how,' the inventor of the Soro process showed that it is still possible for the little guy to make the big bad cartel sheathe the iron fist and extend not only a velvet glove but a velvet glove with some money nestling therein.

" In 1935 Edwin Schuetz was manager of A. G. Oederlin & Co., of Baden, Switzerland, somewhat of a peanut of an industrial enterprise by American standards, but still a profitable producer of a small line of plumbing fixtures and related brass products. That is, it was profitable until the dominating group of Swiss copper fabricators (Swiss Metal Syndicate) in an exquisite demonstration of free enterprise, stabilised rod and bar prices at neat but high level during a period when scrap prices were stabilised at an equally neat but low level. Oederlin & Co. and a few others sweated it out for a while, but after a year or so Herr Scheutz decided to hell with it all, and therewith proceeded to devise the ingenuous Soro process, which converted Oederlin's plant reflow scrap with some pig metal additions into all the bar and rod requirements of the plant.

" By 1937 Herr Scheutz had his Soro equipment running full blast. (The tag, ' Soro ' is what was considered a euphonious mixture of S for Scheutz, O for Oederlin, and RO for ratationsguss or rotational casting).

1. Reviewed in *Metal Progress*, 45, March, 1944, pp. 497-498.
2. *Iron Age*, 153, Feb. 24, 1944, pp. 18-65.

With a couple of induction furnaces, a battery of three 39-in. diameter centrifugal ring casting machines, an old horizontal la he, a metal-cutting circular saw, and a draw-bench, all housed within a medium-sized room, Scheutz proceeded to turn out about 1000 tons yearly of Muntz metal and other brass analyses in rods, bars, forging blanks and rolling ingots, and a spotty supplementary output of bronzes, aluminium and magnesium alloys, stainless steels and a couple of experimental runs on other alloy steels."

All this had the tendency to make the Swiss Metal Syndicate somewhat fidgety, so after a little formal sparring with Oederlin the Syndicate ended up as exclusive licensees of the Soro process in Switzerland (Oederlin excepted) on a rather satisfactory yearly royalty basis. Whilst the syndicate has yet to build or operate a Soro unit, Oederlin turned to other countries and promptly proceeded to make a deal with very large concerns in them. These activities have brought to the Oederlin coffers some £200,000 in licensing fees.

Based solely on the criterion of tonnage of commercial metal produced, the Alcoa D.C. (direct casting) equipment is by far the most successful in operation in America. Every ounce of aluminium and magnesium extrusion billets and sheet slabs produced by the Aluminium Co. of America, with the exception of pure aluminium and the aluminium-manganese alloy, pass through this type of continuous casting unit. These machines are operated under licence by Extruded Metals, Revere Copper and Brass, Inc., Bohn Aluminium, and Tube-Turns.

The author shows the casting of 11 in. dia. billets of 17S in the Alcoa machine by a series of illustrations. For this purpose the molten alloy passes from the furnace down a runner to a cast iron distributor pan, which is equipped with four cast iron nozzles, individually controllable, each of which feeds a casting chamber.

The moulds are simple aluminium (52S) tube sections, 10 in. in length, set into a steel plate framework. 52S alloy has been found the most suitable for this purpose, though aluminium, brass and copper moulds have been used. The aluminium alloy moulds are cooled externally by water sprays or jets. Underneath the moulds there is a hydraulic platform which is lowered as casting proceeds, carrying the billets with it. On leaving the moulds, the

billets are cooled by additional sprays of water. In the machine illustrated four billets are cast simultaneously. The platform descends at about 3 in. per minute and the whole cast takes about 40–50 minutes at which time the billets are some 10 ft. or more in length. At the end of the cast, the distributor pan is removed and the platform is lifted sufficiently to loop crane slings around the billets and lift them from the pit. The machine is then reset for the next cast. With the particular machine illustrated, production is at the rate of about 25,000 lbs. of metal every eight hours, but output will vary considerably depending on ingot size, number of moulds being poured simultaneously and the alloy being cast.

Successful operation of the machine depends on correctly balancing the various factors such as cooling, rate of casting, etc., which affect the quality of the billets produced. It is noteworthy that magnesium-base alloys are also being cast in this machine. In this connection it is mentioned that Alcoa carried out some experiments on the use of a submerged pump to feed the magnesium alloy from the furnace to the machine. These experiments were given up, but similar work is in progress at the works of Dow Chemical Co.

Various Yunghano continuous-casting machines have been operating successfully in America, and it is believed machines of this type are being extensively used in Germany. Since 1940, a number of larger and better engineered Yunghano machines have been built in America, for use primarily in the brass foundry. The Extruded Metals Corp., however, has had a machine in operation for about a year producing aluminium alloy billets up to 14 in. dia. The operation of this machine is shown by a number of illustrations. With this machine delivery speed varies from 5 to 20 in. per min., equivalent to some 100,000 lbs. of aluminium alloy billets every eight hours.

The mould is of drawn copper with a wall-thickness of about ½ in. and about 10 in. long ; it is surrounded by a water jacket. When casting aluminium, an aluminium alloy mould may be used much in the same way as in the Alcoa machine. The molten metal is introduced into the mould underneath the surface of the metal pool, a distributor underneath the metal surface causing the incoming metal to flow radially with the minimum of turbulence towards the mould

face for rapid cooling. If required, a reducing atmosphere can be maintained in the mould above the metal surface.

The special feature of the Yunghano machine is that the mould travels down with the billet for a certain distance and then returns rapidly to its original position, the return being at about three times the speed of the billet. This reciprocating motion of the mould facilitates cooling and also tends to minimise skin cracks. The billet leaving the mould passes through a water spray chamber for additional cooling. The bottom of this chamber is provided with a rubber squeegee seal which prevents the water from running down the billet. The billet, as it emerges from the squeegee, is both cool and dry. The billet then passes through pinch rolls and is finally cut up into required lengths by a flying saw.

As with the other continuous casting processes of this type, cooling of the billet by contact with the mould takes place over a comparatively short distance, the solidifying billet then shrinking away from the mould, with the result that heat transfer is reduced. At this stage the molten metal in the interior may disintegrate the outer skin and it is, therefore, necessary for the billet to pass as rapidly as possible through this critical zone into the spray chamber for further cooling. Coolant working up into the gap between the billet and the mould minimises any interruption of the cooling process and opens the way to higher speeds of operations.

The American Smelting & Refining Co. has had an Eldred continuous-casting unit in operation for the past four years producing large tonnages of oxygen-free copper billets up to 3 in. in diameter. The machine makes use of graphite moulds with no lubrication. Slow casting speed resulting from low rates of cooling is compensated by having a number of moulds. Heat withdrawal is longitudinal and because of this and the slow heat removal, crystal sizes were sometimes enormous. In one instance a copper rod was produced as a single crystal some 32 ft. in length. All this favours the production of metal that is gas-free and very dense with exceptional mechanical properties. The surface of the metal is also excellent. The machine works continuously day and night. The graphite dies have a life of several hundred hours and, when necessary, the die can be replaced without interrupting the casting in the other dies.

Continuous Casting of Steel Ingots

The Williams continuous-casting process for steel ingots and billets has been taken over by the Republic Steel Corp. for extensive experimental investigation. At present suitable types of mould and cooling conditions are being studied. The only other equipment in experimental operation with steel is that designed by N. P. Goss. An experimental unit is being operated at the plant of the American Steel & Wire Co. Difficulties in connection with the cooling of the metal as it passes through the mould has been countered in this process by using a mould made up of numerous sections, each section individually cooled. Particularly interesting is the means provided whereby, as the metal skin freezes and pulls away from the mould wall, a finely divided solid material is introduced through many orifices in the

mould wall. This material is capable of remaining solid during the casting operation and also capable of accommodating itself to the interstices between the cast metal and die wall. In this manner the walls of the die are protected from abrasion and galling, and the congealing metal is also protected from run-outs and abrasion. This material also maintains a heat-conducting contact between the ingot skin and the die wall.. The Goss method also provides for sealing off the top of the mould and introducing above the metal pool an inert or reducing gas to prevent metal oxidation, and also under sufficient pressure to create considerable hydrostatic pressure, if so desired. From casts already made it has been determined that the mould is a feasible piece of equipment, that sound metal can be cast at fair speed, and a very smooth ingot skin can be obtained.

Design of Powder Metallurgy Parts

By M. T. Victor and C. A. Sorg

THE competitive advantages and disadvantages of powder metallurgy as a fabricating process are discussed and consideration is given to those design principles that the engineer should apply to utilize fully the actual advantages of powder metallurgy parts. Because the major applications of such parts include those in which the powder method is used because it provides a special structure or quality not obtainable otherwise, as well as those in which powder metallurgy must compete with other methods, design factors are dealt with which could apply to both groups, with particular emphasis, however, on the competitive-with-other-methods aspect.

As compared with other processes, powder metallurgy involves relatively high raw-metal costs, whereas the material waste from powder metallurgy is virtually the lowest of the competitive fabricating operations. Tool costs for powder operations are among the highest, while labour costs, which are highest for sand-castings, sometimes high for forgings and stampings, are low for automatic operations like die-casting and powder metallurgy. Production rates are high with powder metallurgy, but not quite so high as with die-casting and screw machine fabrication. Tolerances are widest with sand casting: ± 1/32 to 1/16 in., being

normal with small casting, and can be the closest with screw machine operations, where ± 0·0002 in. is not unusual. Powder metallurgy is the next closest, with tolerances of ± 0·0005 in. attainable and even closer on production jobs. Die-casting and stamping come next, depending on part dimensions, both being accurate to ± 0·001 in.

Several limiting factors apply to all classes of powder metallurgy parts. Powder metallurgy is primarily a process of large volumes and most operations proceed at the rate of 200 to 1,600 parts per hour, depending on the shape and size of the part. A new die is required for each part of different design or size and dies must be installed

in presses requiring a "setting up" time of from 1 to 30 hours, depending on the shape of the part. Unit cost, therefore, decreases as volume increases and it is necessary to have minimum runs of 500 to 5,000, depending upon the size and shape of the piece, and the smaller the piece the more volume is required to justify die costs and setting-up charges. The wearing of dies which must be designed and fabricated to very close tolerance, must also be considered. The finest grades of hardened steel are usually used and the various parts are ground and polished to a high degree of accuracy. Holes at right angles to the central hole or to the axis of pressing should be avoided, moulded parts should be made with bevelled edges, and internal angles should have fillets.

In the design of cylindrical parts, a workable relation between the wall thickness and the length of the outside diameter must be maintained and individual powder metallurgy part manufactures have compiled tables of these relationships for their own equipment. Tolerances maintainable are of the order of 0·001 in. per in. on inside or outside diameter and 0·010 in. per 1½ in. in the direction of pressing. In flanged parts sharp corners should be avoided at the junction of the flange and the body, since these are difficult to mould and require additional operations. Similar conditions as for cylindrical parts and flanged parts also apply to profiled parts. With intricate parts, powder metallurgy limitations have to be considered if a practical balance is to be kept between possibilities and cost.

The mechanical properties of most pressed and sintered parts depend, among other things, on their density, which in turn is a function of the raw materials used and especially of the

TABLE I.—PROPERTIES OF SOME POWDER METALLURGY MATERIALS.

Property.	Bronze.			Iron.			Iron Standard.
	Low.	Stand.	High.	Low.	Stand.	High.	
Tensile strength, tons per sq. in.	4·7	6·2	7·4	5·4	7·2	8·9	17·9
Yield-point in compression, tons/sq. in.	3·5	4·9	6·7	9·4	13·4	16·7	22·3
Modulus of rupture, tons/sq. in.	6·7	11·1	15·2	11·1	14·7	21·8	31·2
Porosity, %	29	24	18	34	29	25	24
Apparent density (grms./cc., not oiled)..	5·8	6·2	6·7	5·0	5·4	5·7	5·9
Electrical resistance (michrome–cm)	39	34	29	50	37	33	25
Chemical composition	88–92% Cu 8–12% Sn			92–98% Fe 3–8% Cu			87–93% Fe 8–13% Cu
Melting-point, °C.	Above 816			Above 1,260			Above 1,260
Wear resistance	Good			* Good			Good
Resistance to seizure and galling	Good			Good			Good
Corrosion resistance	Excellent			Fair to good when oiled			Fair to good when oiled
Machinability	Fair (Dry with carbide tools)			Fair (Dry with carbide tools)			Fair (Dry with carbide tools)

sintering temperatures and briquetting pressures used. The properties of some of the regular grades of controlled porosity materials used for machine parts and bearings are given in Table I. Higher density materials and correspondingly high mechanical properties can also be obtained.

Examples of successful applications of powder metallurgy are a roller for machine gun mounts, whose manufacture as a bronze powder metallurgy part saved considerable production time ; a base cover for an aircraft engine mixing valve, whose conversion from machined steel to a pressed iron powder showed considerable improve- ment in cost and output ; and a valve guide for an internal combustion engine made in a graphited brass powder metallurgy part gave several hundred per cent. longer life than when made of former materials.

Copper in Powder Metallurgy
By J. J. Cordiano

COPPER plays an important role in the manufacture of fully 75% of all metal powder parts. Production of copper powder in the United States is estimated to exceed 1,000,000 lbs.; in addition, copper powder is being produced in Europe on an increasingly large scale. The most important methods of production are : (1) Electrolytic deposition ; (2) gaseous reduction of copper oxides ; and (3) atomisation of the molten metal.

Electrolytic Copper Powder

Commercial electrolytic copper powder is produced by electrolysing a solution of copper sulphate and sulphuric acid in lead-lined tanks, using copper anodes and antimonial lead cathodes. Conditions as to current density, bath temperature and composition, are maintained in the cell to deposit copper in a finely divided form on the lead cathodes, from which it is brushed periodically. When sufficient powder has accumulated in the bottom of the tanks, it is removed, placed in a centrifuge, and washed free of electrolyte. The wet residue is then passed through an electrically heated furnace, through which passes a reducing and protective atmosphere, under controlled conditions. The dried powder is then classified, blended to specification and packed in hermetically sealed drums.

References to patent literature, describing various methods of producing copper powder by electrolysis include : Koehler[1], who mentions a method of producing copper powder, using an electrolyte containing in solution 0·5 to 3·5% by weight of copper and 0·5 to 10% by weight of free acid, a bath temperature of 24° to 38° C., an electrode spacing of 3 in.

(76 mm.), a voltage of 2 to 7 v. and a cathode current density of about 12 amp./sq. ft. (1·3 amp./dm.²). Drouilly[2] produces copper powder by the electrolysis of a copper sulphate solution containing the carbonaceous reaction product of glucose and sulphuric acid substantially in colloidal dispersion.

Fitzpatrick and his associates[3] describe a method of producing copper powder using lead-lined wooden tanks ; 6 rectangular copper anodes, providing a surface of approximately 12 sq. ft. (111 dm.²) ; 12 cylindrical copper cathodes providing a surface of approximately 2·5 sq. ft. (23·2 dm.²) ; an electrolyte containing from 2·29% to 2·45% of copper (as copper sulphate) and from 11·32% to 11·43% sulphuric acid ; an average current of 893·73 amp. at 1·50 v. ; an average electrolyte temperature of 129·3° F. (54° C.) ; an average anode current density of 74·5 amp./sq. ft. (8 amp./dm.²) ; and an average cathode current density of 380 amp./sq. ft. (41 amp./dm.²). Gassing at the electrodes provided the only circulation in the cell. The deposit was dislodged by rapping the cathodes, the copper sludge or slime removed to a gravity filter and water-washed free of electrolyte. The washed powder was submerged in water in shallow copper pans and subjected to a vacuum of about 26 in. (660 mm.) of mercury in a cold vacuum dryer. During the vacuum treatment the powder was dried by boiling off the water at 125° F. (52° C.). The resultant product was a finely divided copper powder which passed through a 160 mesh screen and had an average purity of 99·56%.

Fisher[4] provides an apparatus and method for producing electrolytic

copper powder which would result in less current and acid consumption and better efficiency than previously possible. Twenty-one copper plates, each approximately 24 in. (61 cm.) wide, 20 in. (51 cm.) deep, and 0·5 in. (1·3 cm.) thick, are spaced 5⁄16 in. (0·8 cm.) apart in an electrolyte bath maintained at 54° C. and containing substantially 4·5% sulphuric acid, 1% metallic copper or 4% copper sulphate, 8% sodium sulphate and the remainder water. The direct current applied to the end electrodes was approximately 460 amp. at 15·5 v., resulting in a cathode current density of 138 amp./sq. ft. (14·9 amp./dm.²) and a voltage between plates of 0·775 v. In operation, the current was reversed every 12 minutes and sweeps traversed the spaces between electrodes every 4 min. to remove the bulk of the cathode deposits. A pumping arrangement maintained the electrolyte in circulation and at intervals the copper powder was removed from the bottom of the tank.

Reduced Copper Powder

The raw materials used in the gaseous reduction process are mainly copper oxides, scales, copper scrap, and chemical precipitates, capable of being cleaned and converted to oxides of copper by roasting. These oxides are comminuted and reduced to the metal by heat-treatment in continuous-type furnaces with reducing and protective atmospheres. Hall's patent[5] gives a description of an apparatus and method for continuously reducing copper oxides in a controlled atmosphere furnace. The oxide powder, which usually contains 60 to 90% Cu_2O and the balance cupric oxide, is fed on an endless belt, which is furrowed to facilitate the breaking down and pulverising of the friable mass of reduced copper. An average belt speed of 8 ft./hr. is maintained through a 35 ft. heating section and an 18 ft. cooling section of the furnace. The furnace temperature is gradually stepped up from 400° C. at the first stage to 550° C. at the third stage, with the fourth and final heating stage at 400° C. A representative atmosphere having good reducing qualities had the following composition : carbon monoxide 32%, hydrogen 33%, methane 12%, other hydrocarbons 8%, nitrogen, carbon dioxide, etc, 15%.

The direction of flow of the reducing gas is maintained counter current to the

From paper presented at at general meeting of the Electrochemical Society, April, 1944. Preprint 85-4.
1 W. Koehler, U. S. Pat. 1,777,371 (Oct. 7, 1930).

2 E. Drouilly, U. S. Pat. 1,799,157 (April 7, 1931).
3 E. Fitzpatrick, C. W. Clark, and P. A. Tiernan, U.S. Pat. 1,804,924 (May 12, 1931).
4 J. S. Fisher, U. S. Pat. 2,216,167 (Oct. 1, 1940).

5 E. J. Hall, U. S. Pat. 2,252,714 (Aug. 19, 1941).

direction of travel of the charge. The fritted copper mass is scraped from the conveyer belt as it leaves the cooling section of the furnace and is discharged into a saw tooth crusher for pulverisation.

Atomised Copper Powder

Ingot copper is used in the production of atomised copper powder, which generally is composed of globular or spherical particles. In commercial production, the molten metal flows as a thin stream through an orifice and is dispersed by high velocity jets of air. The minute particles are quenched instantaneously by this action and oxidation is confined to a very thin transparent film on the surface of the particles.

Best[6] describes a process for atomising molten metal and congealing the resulting drops to form solid particles. The metal is maintained at 50° to 100° C. above its melting point and directed vertically downward through a discharge tube. An oxy-acetylene flame is played on the lower extremity

6 G. E. Best, U. S. Pat. 2,308,584 (Jan. 19, 1943).

of the discharge tube to prevent congealing or variation in flow of the metal. The thin stream of metal is directed to flow slightly off centre into a high velocity U- or V-shaped air trough, where it is dispersed and congealed. The air trough is non-converging, travels at right angles to the flow of metal, encloses the molten metal, and is formed by forcing cold air at 75 to 180 lb./sq. in. (5·3 to 12·6 kg./cm.²) through orifices disposed to form the U- or V-shape. The atomised metal powder is collected in a conventional collecting system such as a settling chamber, followed by a cyclone or bag room.

In the manufacture of all three types of powders extreme production control must be maintained to insure a uniform product. It is a relatively simple matter to produce a copper powder, but the manufacture and maintenance of such powder to close specifications has required years of patient research and development work in evolving methods, equipment and technique.

cementite, the effect of Mo both on the rate of nucleation of the constituents formed and on the rate of diffusion of carbon, all of which functions may act independently.

Previous work indicates that at 1050° F. the rate of diffusion of carbon in austenite with 0·80% Mo is about 20% of its rate in austenite of plain carbon steel, whilst the present work demonstrates that 0·77% Mo increased the time for eutectoid austenite to form by about 28,000. Hence the effect of Mo on the rate of diffusion of carbon is unlikely to be important in explaining why molybdenum increases hardenability.

Molybdenum Estimation in the presence of Tungsten

By H. N. Roy and S. C. Ghose

MOLYBDENUM in steel is generally estimated as sulphide by passing H_2S gas through an acid solution of the steel, but the presence of tungsten in molybdenum steel involves some difficulty in the estimation of molybdenum. WO_3 will be precipitated when dissolving the steel either by $HCl + KClO_3$ or by $HCl + HNO_3$, and it will invariably carry down some of the molybdenum along with it, and the percentage of molybdenum from the filtrate is always on the lower side. This has been avoided by taking advantage of the fact that WO_3 is soluble in a saturated solution of tartaric acid. Molybdenum can then be completely precipitated as sulphide by H_2S.

Procedure.—Steel (2 to 3 g. as the amount of molybdenum is high or low) is dissolved in 50 c.c. of HCl (1·1). When the steel is dissolved 50 c.c. of 20% tartaric acid solution or 8–10 g. of solid tartaric acid are added to it. The introduction of a few c.c. of HF at this stage is all the more advantageous as it will be an additional help in keeping WO_3 in solution. The solution is heated to boiling and pinches of $KClO_3$ are added from time to time when the steel will go into complete solution and a clear liquid will be obtained. H_2S gas is rapidly passed for 10 minutes, when MoS_3 will be precipitated. It is filtered and washed with H_2S, water and warm tartaric acid solution (5%) and finally

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The Effect of Molybdenum on the Isothermal Sub-Critical Transformation of Austenite in Eutectiid and Hypereutectoid Steels

By J. R. Blanchard, R. M. Parke and A. J. Herzig

DEPTH-hardness depends upon the rate of cooling of the austenitised steel and the rate of transformation of austenite, and although the first of these factors is limited by the thermal properties of the steel, the second factor may be varied by the control of composition, hence the principal function of alloying elements is to control the temperature of transformation of austenite. For optimum use, therefore, it is necessary to understand the function of alloying elements in the decomposition of austenite at constant subcritical temperatures.

The present investigation was carried out to determine the effects brought about by molybdenum on the isothermal transformation of austenite in eutectoid and hypereutectoid steels. The principal effect of increasing amounts of this element is to shift the S-curve to the right above 900° F. and to produce a bay in the region of 1100° F., the latter being the result

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of the much greater effect of molybdenum on the rate of transformation of austenite to pearlite than the rate of transformation to bainite. The "bay" in the curve also separates those structures which are predominantly pearlitic from those predominantly bainitic.

Commercial austenitisation of Mo-steels frequently results in heterogeneous austenite, and if this is of the type evidenced by undissolved carbides, these, if in sufficient quantity nucleate transformation in advance of grain-boundary nucleation at temperatures above 1100° F.

In both types of steel examined, Mo increases the interlamellar spacing of pearlite at 1200° F. to a notable extent.

Though not completely understood, the role of Mo, like other elements, in retarding the decomposition of the austenite, is believed to depend on phenomena involving diffusion, including the rate of diffusion of Mo, the partition of Mo between ferrite and

washed with hot water. The precipitate is ignited at 600° and weighed as MoO_3 (impure).

The oxide is then dissolved by boiling with ammonia; MoO_3 will go into solution and iron, etc., will remain behind. It is filtered, washed with warm ammonia water, ignited and weighed. This weight should be deducted from the first weight of impure MoO_3. The difference multiplied by 66·6 and divided by the weight taken will give the percentage of Mo.

High Speed Steel	% Mo present	% Mo found
1	5·30	5·18
2	5·12	5·02
3	4·98	4·80

The whole procedure takes one hour and fifteen minutes.

Production Applications of Flash Welding

FLASH welding is a form of butt welding in which the two parts to be joined are connected to the secondary terminals of a low voltage, high current transformer and brought into close contact. The two mating surfaces should be of the same shape and approximately of the same cross-sectional area, but apart from being reasonably flat, no special surface treatment is required. Arcing or flashing will occur when the current is switched on and the material in the contact area will melt rapidly. The work is held in a special clamp which causes the two mating parts to approach at a gradually increasing speed during this process, thus ensuring a relatively constant flashing current.

At the end of the period, the speed of approach is suddenly increased, causing a large rise in the welding current to the short circuit value. During this so-called upset period, the mating parts are pressed together with considerable force (10,000 lb. to 20,000 lb. psi. of cross-section of weld), the total amount of travel being limited by stops on the clamps. The current is usually cut off in the early stages of the upset period, the weld then cooling under clamped conditions. (Clamps are water-cooled.)

If, however, very thin tubes are welded, the current must be cut off slightly before the upset operation, so as to prevent overheating.

It will be noted that the flash butt-welding process is characterised by a definite shortening of the mated materials which is the sum of the relative approach during the flashing and upsetting periods. In contradistinction to electric arc or gas welding no material is added during the process.

On the contrary, during the flashing, material is actually burned away, whilst during the upset we have a compacting process similar to forging. This compacting is accompanied by a

R. Milmoe, SAE National Meeting, Jan., 1943. By courtesy of R.T.P. 3, Ministry of Aircraft Production.

squeezing out of oxidised metal and other impurities at the joint, which is one of the main reasons for the high quality of the resultant weld. (100% joint strength.)

If the final use of the parts is to be in the normalised condition or at comparatively low heat-treatment (e.g., up to 140,000 psi.) all the components may be final machined before welding. Moreover, since the flash welding process does not result in a warped assembly and the total approach in the welding machines can be accurately controlled, the completely finished components will join up in a finished assembly having a tolerance of ± 0·01 in.

The process is thus especially attractive for tube joints in aircraft construction.

In the case of normalised SAE 4130 tubes, the weld is fully equal to the parent metal as regards static strength, tensile fatigue and tension impact.

After welding, the parts may be heat-treated to any desired strength without reducing the strength of the weld area.

The production of consistently good welds depends on :—

(1) Suitable preparation of the parts before welding.

(2) Proper adjustment on welding machine and consistency in operation of automatic features of welding machine.

(3) Satisfactory inspection technique.

1. Mating surfaces should be parallel and square, but not smoothly machined or polished. A somewhat rough surface resulting from a power saw or cut-off wheel is recommended.

Surfaces should be clean and free from scale, and this also applies to the parts held in the clamps (current lead-in).

2. The proper machine adjustment is a matter of experience. Upset pressure and upset travel and instant of current cut-off are of special importance.

3. The best available inspection method is the close control of the flash welding equipment and the process.

At the beginning of each new run, three specimens are tested to destruction and one examined microscopically. Subsequent samples are taken after each 25th weld. No strength tolerance below the test load is permitted.

The final machine adjustments are recorded so that they are available when setting up the particular machine for subsequent lots of the same part.

Structural Features of German Aircraft

By D. M. A. Leggett and J. H. H. Davison

THE authors deal with materials used in German aircraft. They state that in present-day types about 70 to 80% of the total structure weight is of aluminium alloys, about 4 to 5% of magnesium alloys, and something under 8% of steel. The remainder is made up of such items as rubber tyres, safety glass windscreens and fibre tanks. Of the total amount of aluminium used, by far the largest proportion is in the form of sheet, or sections formed from sheet. With few exceptions the only extrusions used are the spars, and even here they often consist of a built-up combination of sheet and extrusions. Thus, of the total aluminium alloy employed, about 80% is in sheet and 10% in extrusions, and the remainder in forgings and tubes. Although recently there has been some evidence of an increase in the use of extrusions, the proportion used is still considerably less than on similar British types and constitutes a striking difference between production methods in the two countries.

The properties of some of the high-strength alloys used showed that the materials had been given an elevated temperature ageing treatment and were similar to D.T.D. 364A.

The magnesium employed in current German types appears for the most part in forged engine bearers, in cast-wheel hubs, and in tail-wheel forks. Various control levers are of cast magnesium, while magnesium sheet is used for small detachable panels.

Surface protection against corrosion has always been used to a limited extent in German aircraft and this amount has decreased still further during the course of the war. It is known that very frequent inspection and cleaning now take the place of surface protection.

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